

Amedeo Avogadro (1776-1856)

Professor in the University of Turin, Italy

Renowned for formulating the fundamental principle
of modern chemistry
known as Avogadro's principle.

From a photograph of a statue
erected to his memory at Turin.

Chemistry

A TEXTBOOK FOR COLLEGES

By

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Preface

THE PREFACE to a book is like the overture to an opera or the approach to a mansion; it should stimulate pleasant anticipations of what is just ahead. Yet, after all, one must hear all of an opera to appreciate its beauty; must live within a mansion to realize its comfort and harmony; must study a textbook to appreciate its excellence and perceive its defects. Even so, the overture and the approach do foreshadow in a general way what is to follow, and a preface may touch upon some dominant ideas of a book.

From the beginning the authors have stressed the particle nature of matter and the incredible number of particles in the smallest quantity of matter with which the chemist can work. They have freely used the Avogadro number to emphasize this concept. To assist the student, several pages of arithmetic have been inserted in the text, for even college students are sometimes deficient in their mastery of this one of the three R's. The accomplished student will be pleased to find pages he can omit.

The great simplification in the treatment of atomic weights which is achieved by a preliminary approach through the positive ray method seems to the authors to be a most worth-while innovation in teaching technique. Once the student has acquired a working knowledge of atomic weights, molecular weights, and simple formulas, he is far better prepared to understand the seemingly puzzling explanation of how the chemist deduces values for atomic weights.

The early emphasis upon the particle nature of matter, and the preview of the nature of these particles, are intended to serve the student as a guiding thread of simple but basic theory to tide him over until these important topics can be developed more fully in later chapters.

The text includes rather more organic chemistry than is usual. Relatively few students go beyond their first year in chemistry, and most of the materials that attract their attention in daily life are organic materials.

The authors have endeavored to add interest to the treatment of the metals by assembling them in rather large groups based on their electromotive activities and the general plan of their metallurgy

rather than on their periodic placement. Similar compounds in each of such groups can then be treated as a group, and much memory work is saved.

Credit for pictorial illustrations is given in connection with the illustrations themselves. It is not possible to specify individual indebtedness to the large number of associates and friends who have been of the greatest assistance in preparing the text.

THE OHIO STATE UNIVERSITY
PURDUE UNIVERSITY

THE AUTHORS

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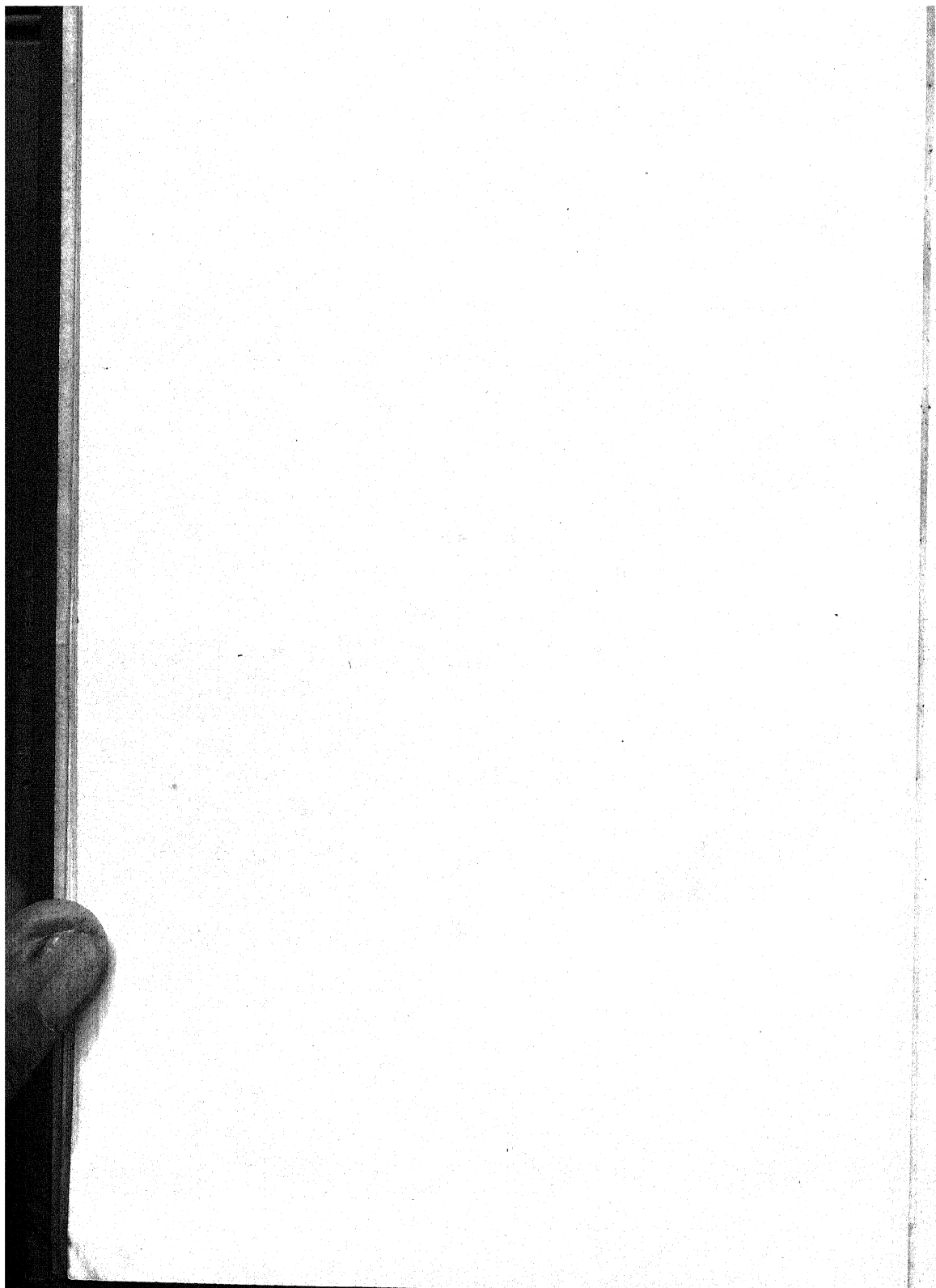
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TABLE OF ELEMENTS

Inside back cover

Chemistry—A Textbook for Colleges



CHAPTER 1

The Adventure of Modern Science

Are the days of adventure past? When someone speaks of the days of adventure, the mind turns to the travels of Marco Polo, the voyages of Columbus or Magellan or Drake, the overland trail of Lewis and Clark or of Livingstone, the polar quests of Peary or Scott or Byrd. Such adventures are nearly past. The antarctic is a vast and lonely place of ice; there are great swampy forests in Brazil, mysterious fastnesses in Tibet, and some little-explored islands in the oceans. But most places of the world are rather well known to us, and nothing very new or strange is likely to be found in the still unexplored regions. If we further ask, What has driven these adventurers on their way? we shall finally agree that it was *curiosity*.

Science the great modern adventure. But there are adventures other than geographical ones, other unknown regions to explore besides those of new continents or ocean islands; and of these the fields of science are among the most fascinating. In the domains of science are continual quests in search of an understanding of the world in which we live, and these quests are adventures just as alluring and just as daring as those that led the great explorers into the remote places of the world. And what leads the man of science into his adventure? Again, it is his great curiosity to know more about some curious facts of nature that neither he nor anyone else understands at the present time. He is a true adventurer into the unknown.

In addition, he has a second motive. He knows that the discovery of new facts, a better understanding of the nature of the material world, the production of new materials from the crude ones found in nature, the increasing comprehension of the mechanics and chemistry of living organisms that make life possible, all contribute, when properly used, to more comfortable and healthful human living.

The scientist and the inventor. The scientific adventurer is moved chiefly by curiosity. Other minds lay hold of the discoveries of the scientist and turn them to economic account, and we call these men *inventors*. As time has gone on and great industries based on discoveries have arisen, the scientist and the inventor often work side by side and pool all they know and can discover in the interests of

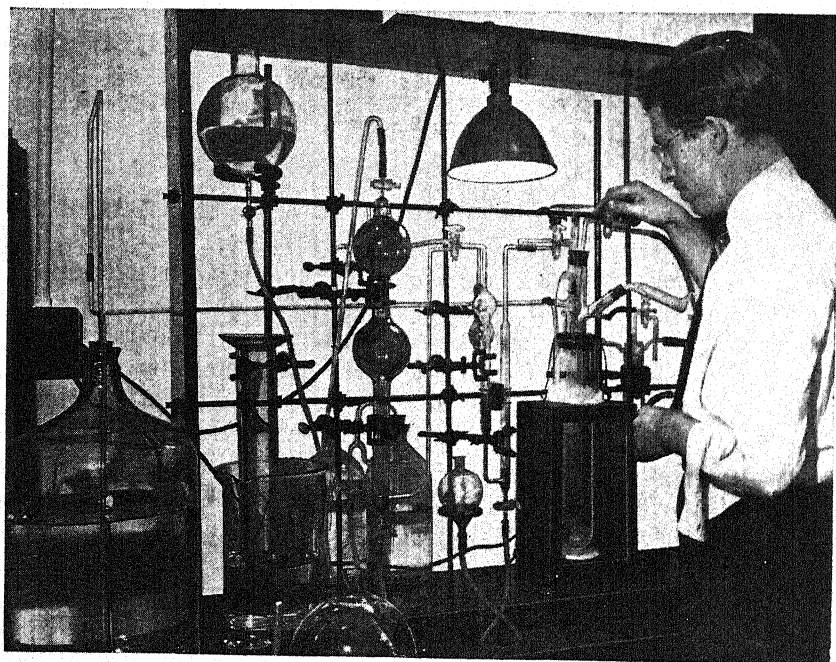


FIG. 1. *A Young Scientist Pursues His Adventures in the Domain of Chemistry*

industry. Sometimes the scientist is also an inventor ; less often the inventor becomes a scientist.

Science a recent adventure. In a delightful essay Henry Morley writes of the times of Vesalius (1514–1564), who has often been called the father of anatomy, as “Anatomy in Long Clothes”; for those days were in reality the babyhood of modern anatomy. In a modern sense few of the sciences were able to stand on their feet and walk easily more than one hundred and fifty years ago, and this is a very short period in the recorded history of civilized man. A baby requires some years of growth before it comes of age, and so it has been with science. Beginnings, instincts of interest in all sorts of nature’s curiosities, steps here and there, the discovery of many isolated facts, and the invention of the calculus by Newton and Leibnitz, marked the babyhood and adolescence of science ; but most of the sciences came of age and began their great adventures about the turn of the nineteenth century — say about one hundred and fifty years ago.

Chemistry one of the great adventures. Of all the continents of unknown boundaries, chemistry (and its twin science physics) is one

of the most alluring for adventure (Fig. 1). There are many reasons for this. Every day and on all sides chemical puzzles meet the adventuring eye. Why does ethylene gas speed up the ripening of green oranges? How does chlorophyll in the presence of sunlight seize upon water and carbon dioxide and from them manufacture sugars and starches? Why does the admixture of some cobalt and tungsten with steel keep it from rusting? How does a wire conduct the electric current? Why do green leaves turn red in autumn? How can fertility be returned to a wornout soil? Every day one asks, Why and how? and to many of these questions chemistry gives an answer to the adventurer or will give an answer someday.

More than that, chemistry underlies most of the sciences. The adventurer in physiology or any of the biological sciences, in geology, in astronomy, in the problems of agriculture, finally comes to the point where he must follow a chemical trail if he is to go farther in his adventure.

Most of the industries have a foundation in chemistry, and they urge the chemical adventurer to start in their factories in his quest for new things. If you should make a list of all the articles in your home, you would find that nearly all of them owe their utility, their durability, their beauty in some way to the adventuring chemist; and they are still far from perfect.

How does the chemist prepare for his adventure? The chemist prepares for his adventure like any other wise explorer. Those early captains got the best ships they could command, manned them with hardy sailors, provisioned them with abundant stores both of food and of repair supplies, looked to their means of defense and (in later years) to a supply of lime juice to ward off scurvy. No such provisions are required for the adventuring chemist. Instead he must equip himself with all the available information about the region in which his quest is to lie; and he must patiently acquire skill in experimentation, just as the sea captain must master the navigation of his ship. The chemical courses of schools and colleges, the libraries they support, the laboratory exercises they require, together with a discipline in clear thinking, constitute the equipment for the adventure that lies before the young chemist.

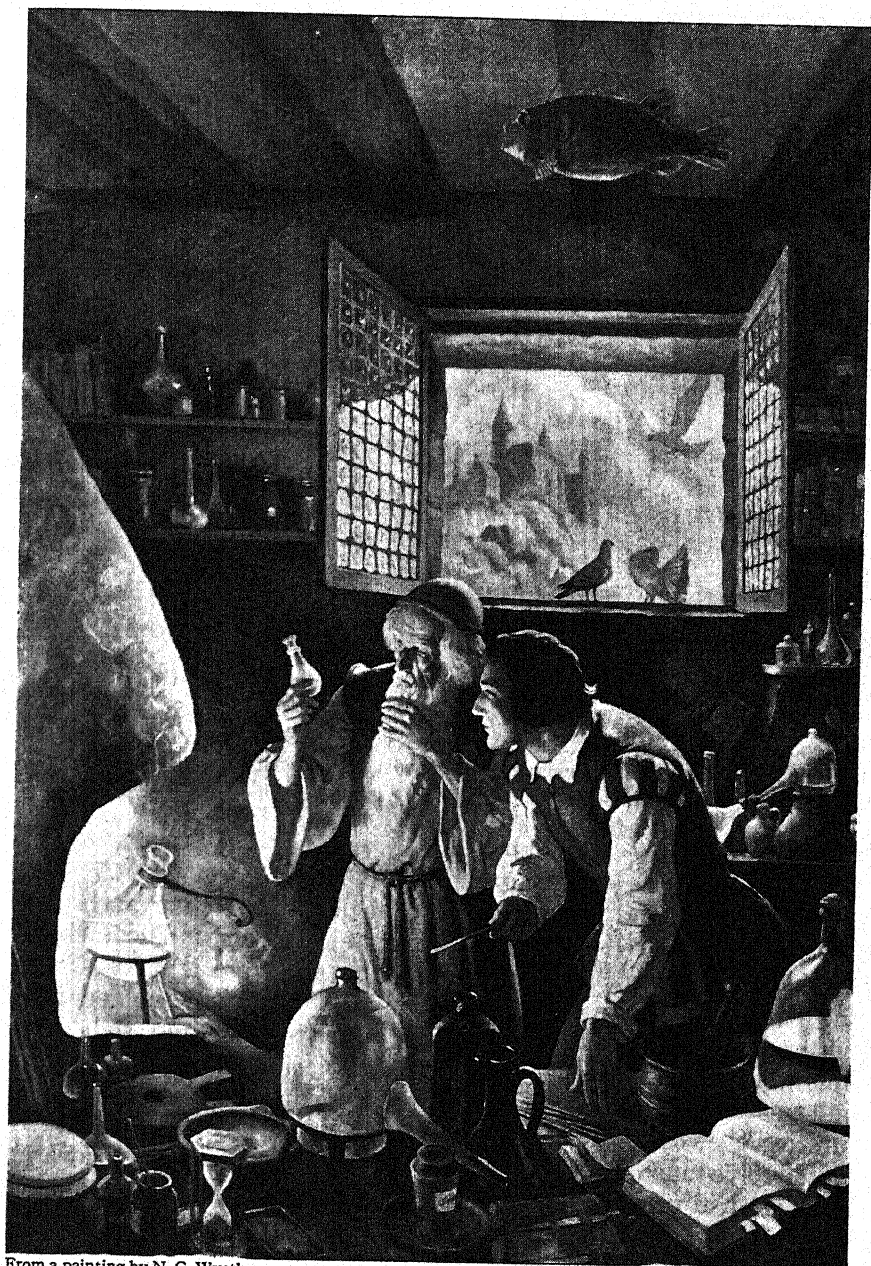
How does the chemist enter upon his adventure? The captain-adventurer must know what he seeks before he starts, and so too must the chemist. He starts with some strange fact or some chemical occurrence that neither he nor his fellow chemists understand, and he seeks an explanation to satisfy his curiosity and to add to the sum total of knowledge. He knows that if an answer is found, it will

come through experiment alone. So he contrives cunning experiments designed to bring to light an explanation of the singular fact or occurrence, and if possible to find a relation with other facts or occurrences. If he is successful, he may be able to establish a *law*. Robert Boyle was struck with the fact that air is elastic. He experimented with compressing a measured volume of air by known weights (pressures) and finally found a relation between the volume of the sample of air and the pressure upon it caused by the weights. This relation is a law of science: The volume of a measured sample of air varies inversely with the pressure placed upon it.

Or the experiments of the chemist may lead to a leap of the imagination about the explanation of the fact or the occurrence that is the object of the quest. John Dalton carried out experiments about some puzzling facts of the composition of compounds, and made the imaginative guess or hypothesis or theory that these facts could all be explained if it is assumed that a compound is in reality made up of minute atoms combined in very definite ratios by number.

When the adventuring chemist arrives at a law or suggests a theory, both he and his fellow chemists strive to test these conclusions by all possible experiments. In the course of these testing experiments new and unexplained facts or occurrences come to light, and the quest about them begins in turn. The stages in the quest, — the noticing of unexplained facts, the formulation of laws that state relationships or the leap of the imagination to probable explanations, the testing of both theories and laws by critical experiments, the discovery by this means of new problems, — these stages taken together constitute what is called the method of science. It is the program of the adventuring chemist.

The alchemist. It may be argued that chemistry began long before 1800, for did not the alchemists toil in their workshops during the thousand years before that date? It is true that the alchemists worked with chemical materials and incidentally discovered many chemical facts, but they had before them one and only one definite objective — to transmute some of the common metals into gold (Fig. 2). They had no adequate equipment in knowledge or experimental skill for this adventure, nor much interest in the facts brought to light by their efforts; and the one objective on which they staked everything happened to be almost impossible of attainment. It was almost as though the astronomers of the ages had directed all their efforts toward communication with the inhabitants of Mars to the exclusion of all other interests. The resources of modern science have been able to prove that the transmutation of



From a painting by N. C. Wyeth

Hercules Powder Company

FIG. 2. *An Alchemist Working in His Laboratory*

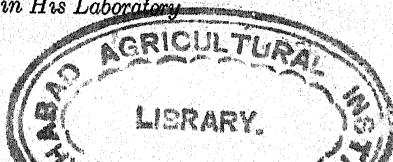




FIG. 3. *A View of the General Office of Chemical Abstracts — a Journal Published by the American Chemical Society*

This journal prints abstracts of all articles containing new information of chemical interest. The number of journals whose articles are abstracted is approximately 3200, and the number of abstracts printed annually is about 65,000

the metals can be accomplished but certainly as yet not on the economic scale for which the alchemist hoped.

Ancient arts and crafts. In very ancient times many arts and crafts were practiced that depend on chemical actions. The ancients were able to extract some six or seven metals from their ores, and the palaces of Crete had lead plumbing. Clay was molded into pottery, baked, and even glazed in very early days; sand, soda, and lime were melted together to form glass; various fabrics were dyed and treated with mordants that gave a variety of colors; crude mortars and even cements made from volcanic lava were in use. All these arts involve much chemistry, but of this the ancients were not aware. Each art had primitive and probably accidental beginnings and was handed down from father to son with slow improvement through the ages. There was no real understanding of any of them.

Scientific societies. One reason why science was so late in coming of age was the fact that most of the early workers worked alone and

in seclusion. They had to depend for their information on hand copies of a few manuscripts that claimed authority. The invention of the printing press brought about wide circulation of many books, but there was no considerable impact of mind on mind in personal contacts. Travel was slow and difficult. Presently universities were founded, and societies of scholars were organized that brought science adventurers together for personal acquaintance and for sharing ideas about problems.

Today there are societies of this kind in every division of scientific endeavor, each of which has a journal devoted to its particular interests. The American Chemical Society is one of the largest of these. It has a membership of over twenty thousand and publishes five separate journals for the benefit of its members. The remarkable advance of science in recent years is due in no small degree to the teamwork resulting from membership in these societies (Fig. 3).

Reading References*

BOYD. *Research*. A most interesting and readable book on the general subject of research.

DAVIS. "Primitive Science, the Background of Early Chemistry and Alchemy," *Journal of Chemical Education*, Vol. XII, pp. 3-10.

FOSTER. *The Romance of Chemistry*. Chapter I, "Alchemy and the Rise and Development of Chemistry," will be found of interest.

FRENCH. *The Drama of Chemistry*. Chapter I gives a brief account of the early history of chemistry.

LEONARD. *Crusaders of Chemistry*. Chapter III treats of alchemy.

OESPER. "Alchemy: Folly or Wisdom?" *Journal of Chemical Education*, Vol. VII, pp. 2664-2674. An interesting and well-illustrated article.

READ. *Prelude to Chemistry*. A book of three hundred pages, recommended for those who wish to learn more about the alchemists.

* A list of the books and journals to which reference is made in this text, together with the names and addresses of the publishers, will be found in the Appendix.

CHAPTER 2

Matter and Energy; Units of Measurement

Introduction. Man lives in a changing world. History records the changes in modes of living, in political boundaries, and in human institutions. We hear that the present economic ailments result from changes in our methods of production and distribution. Common experience teaches us that all material things with which we are acquainted constantly undergo changes of some sort. The metals rust away; the solid rocks weather and disintegrate; the most imposing buildings finally crumble into ruins. While the variety of such changes in nature is almost without limit, the men who have pondered upon these alterations have recognized a duality common to all of them — the *matter* which undergoes change and the *energy* which causes the change or results from it. Matter and energy are thus the two fundamental things in terms of which we seek to describe and explain our material environment and the changes it undergoes.

Many of these changes bring about the formation of substances which are at once recognized to be different from the original ones. When iron rusts, the rust is evidently entirely different from the iron. When a lump of coal burns, the invisible gases and handful of ashes into which it is converted bear no resemblance to the coal.

The science of chemistry. The science of chemistry has for its objectives the accurate study of the composition of matter and of the transformations which material things undergo, the causes that occasion these transformations, the energy changes that accompany them, and the laws in accordance with which they take place. Chemistry is therefore very intimately concerned with both matter and energy, and it will be of great advantage if at the outset we get clearly before us some fundamental conceptions in regard to them.

MATTER

Weight and mass. Since matter is so fundamental, we find difficulty in accurately defining it because there is nothing more fundamental, nothing simpler, in terms of which to construct a definition. We sometimes say that *matter is anything which occupies space*

or possesses mass or weight. Such a statement is helpful but not completely satisfying. Space, like matter, defies definition. Often the

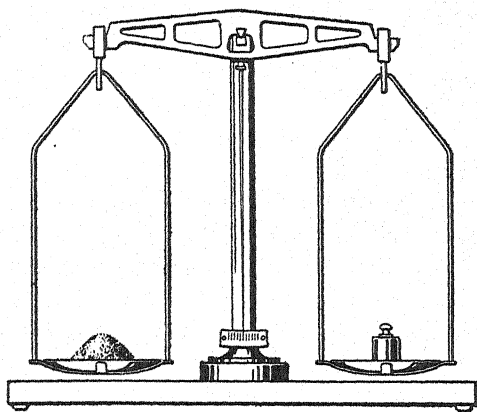


FIG. 4. Chemical Balance

best definition that we can give for a thing is to tell all that we know about it. Sometimes, too, we can clarify our thinking a great deal by making our observations of a thing as accurate as possible, namely, by making *measurements*. Such a quantitative treatment of physical and chemical behavior may frequently bring to light significant points which were not suspected at all on mere qualitative examination.

Measurement of weight and of mass. Instruments for measuring weight are known as *balances* (often called scales). Balances are of two types: (1) the chemical balance (Fig. 4) and (2) the spring balance (Fig. 5). With the chemical balance a given sample of matter, on the left-hand pan, is "balanced" against standard weights on the right-hand pan. With the spring balance a true scale is constructed by observing the extent to which standard weights "stretch" a spring. Subsequently the weight of an object is determined by reading on the scale how far it stretches the spring.

The difference between *mass* and *weight* may be illustrated by the different behavior of these two types of balances. Suppose for the moment that we, like the characters in the writings of Jules Verne or H. G. Wells, are able to make a trip to the moon. We take with us an object previously weighed with a chemical balance on the earth and proceed to weigh it on the moon, where the gravitational attraction is only one sixth that on the earth. Since the attraction of the moon for the weights (on one pan) is exactly the same as for the object being weighed (on the other pan), the chemical balance would indicate the weight of the latter to be the same as measured on the earth.

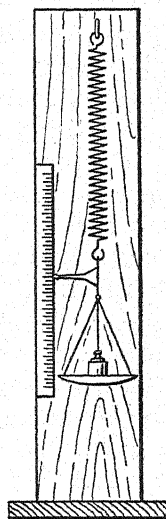


FIG. 5. Spring Balance

In the case of the spring balance, however, the moon's attraction for the object (being one sixth of the earth's attraction) would cause the spring to stretch only one sixth as much as on the earth. Since we feel sure that the actual stuff of which the body is composed, or its matter, has not been altered by this change in locality, we desire a concept of something more fundamental than weight, something of which the quantity is not dependent upon gravitational attraction. This actual stuff, which does not change, is called *mass*. The weight of a body, while not the same as its mass, is, at any one place, *proportional* to its mass. For the practical purposes of the chemist, here on the surface of our earth, we may use the two terms interchangeably, as long as we understand the distinction.

We may also set up another definition of mass that is free from the difficulty of variable gravity. We know that every material body possesses *inertia*. By this we mean that if the body is at rest, it will take a force to set it in motion; and if it is in motion, it will take a force to stop it. We can measure this force in any given case, and so measure the inertia of the body. *The mass of a body is that property that gives it inertia*. If we measure the force that overcomes inertia, we are measuring the mass of the body. If, however, we employ the *force of gravity* for this purpose, we get a *variable* result that we call the weight of the body. This variation arises, of course, because the force of gravity on the earth's surface varies slightly with altitude and latitude.

Conservation of mass. Since the outward form and condition of matter are constantly changing, it would perhaps seem possible that its mass is also undergoing variation. The mass of a lump of coal is certainly much greater than that of the ashes which result from its burning. If, however, we collect the gases formed and take into account all the materials concerned in the burning, we find that the total mass remains unchanged. All our experience goes to show that this is true and that *in all ordinary changes in matter the total mass is neither increased nor diminished*. This generalization is known as the *law of conservation of mass* (Fig. 6). We shall see later that under some rare conditions the mass does change.

The properties of substances. By the term *properties* is meant all those marks or characteristics by which a given substance is identified. Many of these properties are designated by words in common use, such as *color*, *hardness*, *luster*, *transparency*, *solubility*, *melting point*, and *boiling point*. Others are not so obvious to an untrained observer; among these are *density*, *refractive index*, *viscosity*, *conductivity* (for heat and electricity), and *crystalline form*.

All these properties, however, are greatly modified by the physical conditions under which they are observed, especially by the temperature and the pressure. Thus, red oxide of mercury becomes nearly black when heated, but recovers its original color when cooled. All liquids decrease in density with rise of temperature, and thus the warmer liquid tends to rise to the top. Practically the only known exception to this rule is found in the behavior of water in the temperature range from 0° to 4° , where the density *increases* with rising temperature. All gases may be converted into liquids by pressure at sufficiently low temperatures; and the boiling point of a liquid, as well as its freezing point, depends upon the pressure.

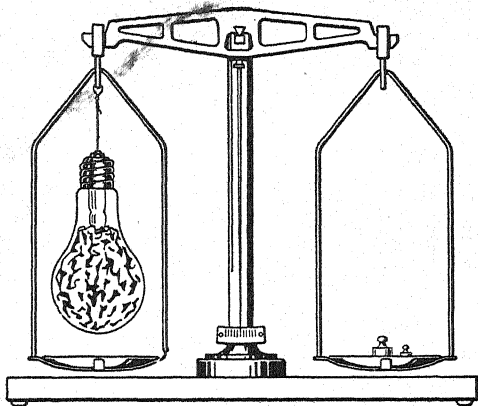


FIG. 6. A Photoflash Bulb

The bulb contains aluminum foil and oxygen gas. By connecting the bulb with a pocket battery, the aluminum foil is heated and combines with the oxygen with a brilliant flash of light. Experiments show that the weight of the bulb before the flash and the weight after are the same

UNITS OF MEASUREMENT

Introduction. In making quantitative measurements of the properties of a substance it is necessary to employ *units*. For example, to measure the length of an object, we first adopt an appropriate standard, or unit, of length and then see how long the object is in terms of this unit. For all scientific work, and in many countries for all purposes, the system of units employed for measurement is the *centimeter-gram-second* (cgs) system. This system, which includes within itself the metric system, differs in many respects from the English, or *foot-pound-second* (fps) system, to which we are accustomed. It is essential that we understand the differences. From earliest times man has used some kind of units to measure length, area, volume, and weight — for example, the foot, the acre, the quart, and the pound. These are arbitrary units and came into use because of convenience and local custom. The confusion caused by a large number of separate and unrelated systems led the National Assembly of France in 1791 to instruct the National Academy of Sciences to appoint a committee to make recommendations. This committee attempted to devise a system the basic standard of which would be found in nature.

Length, area, and volume. After much study and deliberation, the commission chose as the unit of length the *meter*, which was taken as one

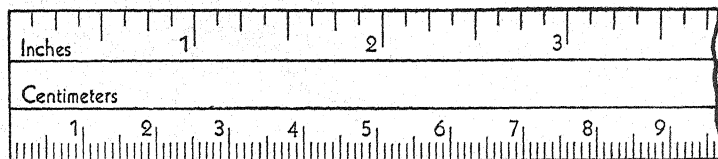


FIG. 7. *The Centimeter and the Inch Compared*

ten-millionth part of a quadrant of the earth as measured from the equator to the pole. For convenience, smaller and larger units were chosen as fractions and multiples of the meter *on a decimal basis* (Fig. 7).

	10 millimeters (mm)	= 1 centimeter (cm)	= 0.3937 inch (in.)
Length	10 centimeters	= 1 decimeter (dm)	= 3.937 in.
	10 decimeters	= 1 meter (m)	= 39.37 in.
	1000 meters	= 1 kilometer (km)	= 0.62137 mile

Units of area (Fig. 8) and volume (Figs. 9 and 10) are obtained by squaring and cubing the units of length.

	100 square millimeters (mm ²)	= 1 square centimeter (cm ²) = 0.155 square inch (sq in.)
Area	10,000 square centimeters	= 1 square meter (m ²)
	10,000 square meters	= 1 hectare (ha) = 2.471 acres
	1000 cubic millimeters (mm ³)	= 1 cubic centimeter (cc) = 0.0610 cubic inch (cu in.)
Volume	1000 cubic centimeters	= 1 cubic decimeter (dm ³) = 1 liter (l) = 1.057 liquid quarts (qt)
	1000 cubic decimeters	= 1 cubic meter (m ³) = 1.3080 cubic yards (cu yd)

Although the measurements which established the length of the meter were remarkably accurate for their day, subsequent measurements have

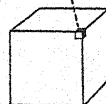
1 square millimeter



1 square centimeter

FIG. 8. *Units of Area*

1 cubic millimeter



1 cubic centimeter

FIG. 9. *Units of Volume*

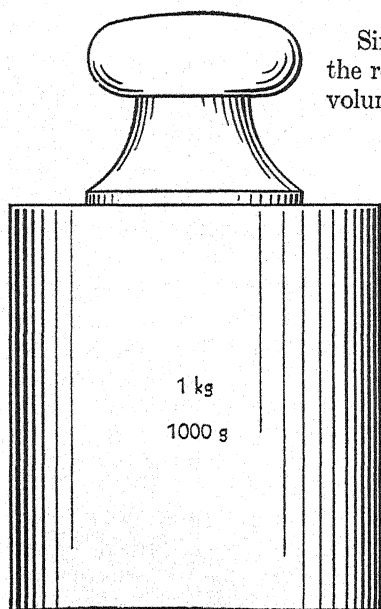
shown that they were not strictly accurate and that the meter is not exactly one ten-millionth part of a quadrant of the earth. Actually the meter is the

distance, arbitrarily agreed upon, between two lines scratched on a bar of platinum-iridium which is deposited at the International Bureau of Weights and Measures at Sèvres near Paris. When comparisons with this standard are made, the bar is maintained at the temperature of melting ice (0°). The governments of most countries have accurate replicas of this standard; that of the United States is in the Bureau of Standards, Washington, D.C. Since the standard meter is known in terms of the wave length of light, it is reproducible even if all existing standards should be destroyed.

Weight. The committee which devised the metric system wished to relate the units of mass and length in a very fundamental way. Hence the standard known as the *kilogram* was taken as the weight of 1 cubic decimeter (1000 cc) of water at its maximum density (4°), and suitable decimal subdivisions of the kilogram were defined (Fig. 11).

Weight

10 milligrams (mg)	= 1 centigram (cg)
10 centigrams	= 1 decigram (dg)
10 decigrams	= 1 gram (g) = 0.0353 ounce (oz)
1000 grams	= 1 kilogram (kg) = 2.205 pounds (lb)



Since it was recognized that the reference of all weights to volumes of water at 4° would be inconvenient,

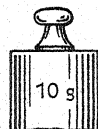
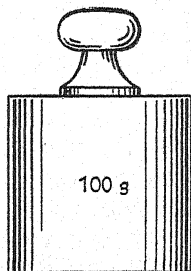


FIG. 11. Metric Weights

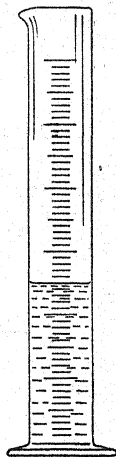


FIG. 10. A Cylinder Graduated in Cubic Centimeters, Used for Measuring the Volume of Liquids

and furthermore that weights can generally be measured much more accurately and conveniently than volumes, a piece of platinum of weight supposedly equal to the weight of 1 cubic decimeter of water at 4° was prepared and, again, deposited at Sèvres. This is known as the *standard kilogram*. The National Bureau of Standards at Washington possesses an accurate replica of this standard. Unfortunately the original measurements were slightly in error, and 1 cubic decimeter of water at 4° does not have a mass of precisely 1 kilogram; and consequently 1 cubic centimeter of water at 4° does not weigh exactly 1 gram, although the difference is very slight.

Milliliter versus cubic centimeter. The unit of volume, the *liter*, was intended to be equivalent to 1000 cubic centimeters, or 1 cubic decimeter, and a liter of water (at 4°) was to have weighed 1 kilogram. However, the error in the original measurement caused the slight deviation mentioned above. To clarify the situation, the liter was defined (1901) as *the volume of 1 kilogram of water at 4°* . One liter thus actually represents 1000.028 cubic centimeters. For this reason many persons prefer to use the term *milliliter* (ml) instead of *cubic centimeter* for a volume equal to one one-thousandth of a liter. Again, the difference is so slight that the two may be regarded as identical for most purposes. The difference amounts to about one half a drop (say of water) in a liter.

Density. The density of a body is the mass of its unit volume, that is, of 1 cubic centimeter. Since this volume of water has a mass of almost exactly 1 gram, the figures which represent the density of a body at the same time tell almost precisely how many times as heavy as water it is. Thus copper has a density of 8.92, which means that 1 cubic centimeter weighs 8.92 grams, and also that, volume for volume, copper is 8.92 times as heavy as water (Fig. 13).

Gases are so very light that their densities must be expressed in numbers which are inconveniently small, that of oxygen being 0.001429. Such numbers are called the *absolute densities*. In describing a gas it is more usual to state the *weight of 1 liter* than to give its density. This is called the *liter-density*. A table giving such weights for a number of gases will be found in the Appendix.

Time. The second, the unit of time, is one-86,400th part of the mean solar day.

Advantages of the cgs system. Among the important advantages offered by the cgs system of units are the following: (1) It has already been universally adopted by scientists, and the records of all measurements in scientific work are reported in terms of its units. (2) There is a very intimate and close-knit relationship among the various units of the system — for example, among the units of length, area, volume, mass, density, time, velocity, force, and energy. (3) The subunits and multiple units are defined decimally, and thus much of the labor and inconvenience of calculation involved in other systems is avoided. (Problems giving practice in the use of the cgs units are listed at the end of this chapter.)

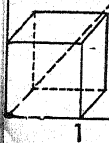


FIG. 12. 1 cm^3 almost exactly equal to 1 ml
 $1000 \text{ cm}^3 = 1 \text{ dm}^3$, almost exactly equal to 1 l
 $1 \text{ l} = \text{volume occupied by 1 kg of water at } 4^{\circ}$

1 2 3 4 5 6 7 8 9 10 cm.

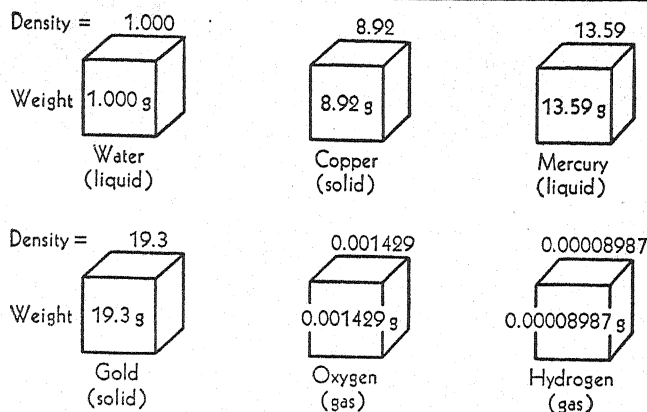


FIG. 13. Weight of 1 cc of Some Well-Known Substances

ENERGY

Definition of energy. Since it has been found that every change in matter involves a change in energy, we must consider some of the characteristics of energy before going on to a more careful study of the variety of changes in matter.

In everyday language we sometimes say that a certain man is full of energy, meaning that he has a great capacity for work. We also recognize the same quality in inanimate things. We realize that steam, highly compressed in the boiler of a locomotive, possesses energy; for we know that when it is admitted to the cylinder of the locomotive, it will push back the piston and move the train. Energy is present in electric-power lines; for a motor connected with them is caused to rotate, an electric lamp to give light, a resistance heater to supply heat. Energy must be expended in raising a block of stone to the top of a building; and, when there, it too possesses energy, for its fall will produce effects which we recognize as being due to the expenditure of energy. *We may therefore define the energy of a body (or system) as its ability to do work.*

Varieties of energy. We recognize energy in many forms, among the most familiar of which are *heat energy*, *electrical energy*, *chemical energy*, *radiant energy* (such as that of light and electric waves), and *kinetic energy*, or the energy of moving bodies. No less important is the *potential energy* which a body possesses by virtue of its position, as in the case of a body raised to a height, or which a body possesses by virtue of its existence in a state different from the normal state, or by virtue of its existence in a state of strain, as in the case of a

stretched spring. Potential energy, when released, may be recovered as other forms of energy.

Units. In dealing with energy, just as in dealing with matter, it is of great practical importance to devise units for the measurement of energy. It is convenient to use different kinds of units for the different kinds of energy. In the case of the mechanical energy required to raise a weight vertically against the force of gravity, the unit of energy (or of work) is the gram-centimeter (g-cm); that is, unit work is performed if a weight of 1 gram is lifted through a height of 1 centimeter. If 1 gram is lifted through 100 centimeters, or if 100 grams are lifted through 1 centimeter, then the energy expended is 100 gram-centimeters. The work required to raise 1 kilogram to a height of 1 meter is 100,000 gram-centimeters, or 1 kilogram-meter (kg-m).

Heat is usually measured by allowing the heat to be absorbed by water. *The calorie (cal), the unit of heat energy, is defined as that quantity of heat which will raise the temperature of 1 gram of water 1 degree (centigrade) at 15°. The kilogram-calorie (Cal) is 1000 times as large as the gram-calorie.*

The thermometer. A thermometer is a "temperature meter," or an instrument for measuring temperature. An alteration in temperature produces marked changes in many properties of matter, such as density, color, and electrical resistance. Such changes have been made the basis for various types of thermometers. The most commonly used type is the mercury thermometer (Fig. 14). It consists of a small glass bulb attached to a long capillary stem. The mercury in the bulb expands when heated and pushes a fine thread of mercury up the stem. The point on the stem where the top of the mercury thread stands when the thermometer is in contact with melting ice is arbitrarily called 0°, and the point at which it stands when the thermometer is exposed to boiling water is called 100°. The distance between, on the stem, is divided into 100 equal parts, known as degrees. This is the way in which the centigrade scale of temperature is constructed. The scale is then extended below 0° and above 100° by marking off degrees of equal length.

There are other temperature scales, such as the Reaumur and the Fahrenheit scale. The relationship of the latter to the centigrade scale is shown in Fig. 14. The equations for converting readings on one scale to readings on the other are as follows:

$$F^{\circ} = (C^{\circ} \times \frac{9}{5}) + 32^{\circ}; \quad C^{\circ} = (F^{\circ} - 32^{\circ}) \times \frac{5}{9}$$

Later we shall be interested in the so-called absolute scale of temperature.

The mechanical equivalent of heat. In 1843 Joule performed a most significant experiment. He arranged the apparatus shown in Fig. 15 so that a slowly falling weight, attached to a cord, would cause a paddle stirrer to churn a body of water. Joule found a constant relationship between the number of kilogram-meters of work performed by the falling weight and the number of calories of heat produced by friction, in the water. These experiments, together with others of various kinds, have demonstrated that mechanical energy may be converted into heat and, conversely, heat into mechanical energy; and further, that there is a constant ratio between the quantities of mechanical energy and heat involved in the transformation. If we use the symbol \equiv , which means "is equivalent to" (rather than the symbol $=$, "is equal to"), this relationship ($1 \text{ cal} \equiv 42,720 \text{ g-cm} \equiv 0.4272 \text{ kg-m}$) is known as the mechanical equivalent of heat.

Transformation of energy. Not only may heat and mechanical energy be interconverted, but all the various forms of energy can generally be freely transformed, one into another (Fig. 16). At least a part of the heat energy of burning coal can be changed into the kinetic energy of a locomotive. The kinetic energy of falling water can be transformed into electrical energy, as is done in hydroelectric-power plants. The electrical energy of the trolley line is readily converted into the kinetic energy of the moving car. In all such transformations a *definite quantity of energy of one kind always gives a definite equivalent quantity of another*. Just as we speak of the mechanical equivalent of heat, we refer to the electrical equivalent of mechanical energy or to the heat equivalent of electrical energy or to the electrical equivalent of heat energy. The relationships among some of the units of energy are

$$\begin{aligned} 1 \text{ cal} &\equiv 42,720 \text{ g-cm} \equiv 4.183 \text{ volt(v)-coulombs} \equiv 4.183 \text{ joules(j)} \\ &\equiv 41,830,000 \text{ ergs} \end{aligned}$$

Conservation of energy. The *experimental* demonstration of the complete interconvertibility, without loss, of the varieties of energy led the great German physicist Helmholtz in 1847 to formu-

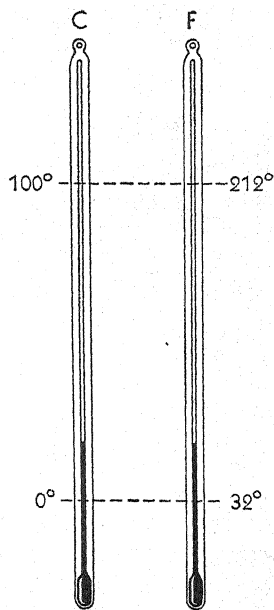


FIG. 14. Centigrade and Fahrenheit Scales Compared

late a law basic to both physics and chemistry known as the *law of conservation of energy*: *Energy, like mass, in all ordinary transformations is neither created nor destroyed.* It is not difficult, however, to alter the distribution of energy between bodies. If a piece of hot metal is dipped into water, the metal is cooled and the water is heated, so that the metal loses energy and the water gains it. When a swinging bat strikes a ball, the latter gains energy, while the bat loses it. There is therefore in a given body no constant quantity of energy, as there is of mass.

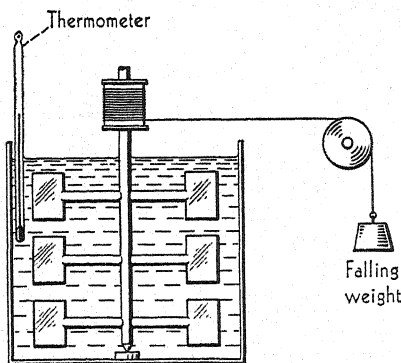


FIG. 15. *Joule's Experiments*

Chemical energy. It will be shown in a later chapter that the process of the burning of any substance in air consists in the union of the substance or its constituent parts with the invisible gas oxygen present in the air. In this process both heat energy and light energy are evolved. If we keep in mind the law of conservation of energy, it is evident that the energy so evolved must be accounted for; and a reasonable assumption to make is that the substance undergoing combustion and the oxygen possess, together, a certain store of energy which in the process of burning is transformed into heat energy and light energy. This form of stored energy is called *chemical energy* and is of special interest to the chemist.

Illustration of chemical energy; chemical affinity. When iron burns in air, the metal disappears as such, and in its place we obtain a hard brittle material black in color. This material is composed of iron and oxygen combined. We must assume that both the iron and the oxygen possess a certain amount of chemical energy which is transformed into heat energy and light energy when the iron burns. It is possible to separate this black material into iron and oxygen again, but experiments have shown that in so doing we must restore to the iron and oxygen as much energy as was evolved when they united. This is what the law of conservation of energy would lead us to expect. The resulting iron and oxygen are now free to unite again with each other, with the same evolution of energy as before.

In some respects the case is similar to the more familiar one presented by falling bodies. When a body falls from a height and strikes

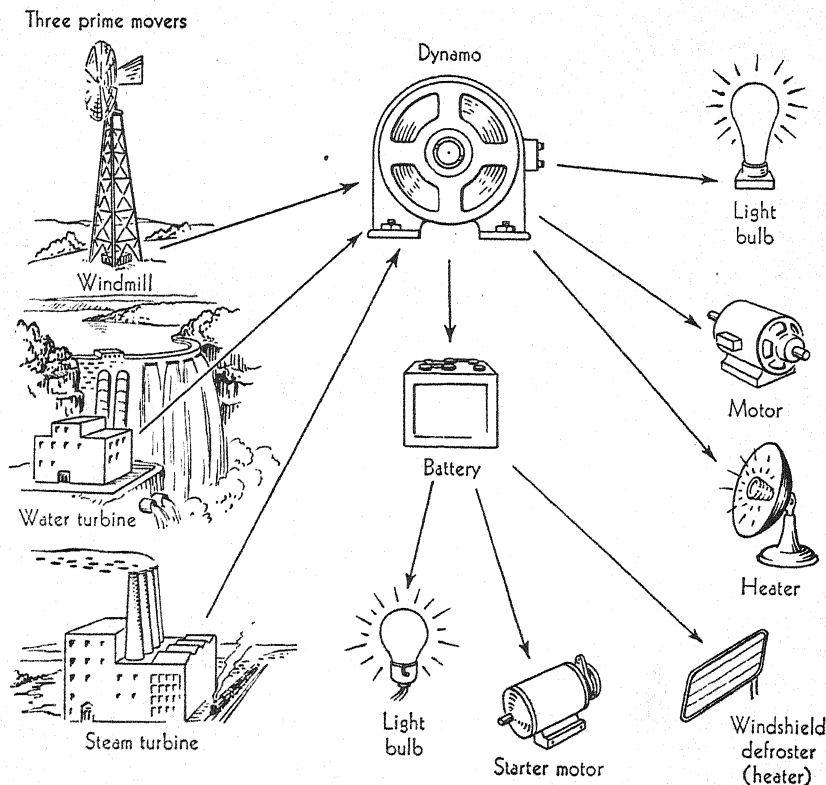


FIG. 16. Some Common Transformations of Energy

the earth, its potential energy is converted into mechanical effects and heat. To restore the body to its former height, work must be done upon it equivalent to the energy set free in its fall. This work is in some way stored within the system (body and earth) as energy, for the body may once more fall with the same effects as before. We do not know how the energy is stored within the system, but we do know that it is, and we name it *potential energy*. We say that the cause of the fall of the body is the force of gravity. Because of this force a body falls toward the earth, and its potential energy changes into *kinetic energy*.

In a similar way we give the name *chemical energy* to that form of energy which becomes apparent when substances combine with each other, and we say that they combine because of the force of *chemical attraction*, or *affinity*. Later on we shall learn more about the present conceptions of the nature of chemical affinity.

The measurement of chemical energy; the calorimeter. In some of its forms energy is very difficult to measure directly, and neither units nor methods for the direct measurement of chemical energy have as yet been devised. In such cases it is necessary to transform the energy into a form more convenient for measurement. Accordingly chemical energy is generally changed into heat energy or electrical energy, and this is then measured in an appropriate unit. The actual measurement of the quantity of chemical energy transformed into heat in a chemical action is accomplished by the use of an apparatus called the calorimeter, a simple form of which is represented in Fig. 17. The chemical action may be arranged to take

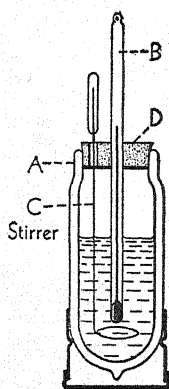


FIG. 17. A Simple Form of Calorimeter

place in solution in a measured volume of water contained in a heat-insulated vessel, such as the Dewar vessel A. This container consists of two glass vessels, one inside the other, which are joined together at the rim only, and the space between them is exhausted by a vacuum pump. A vacuum serves as the best possible insulator to conduction and to convection currents. Further, the inside surface of the outer flask and the outside surface of the inner flask are silvered, so that heat will be reflected from the walls and not absorbed. As an added precaution the vacuum-jacketed vessel is stoppered with a thick plug D of nonconducting felt or cork.

The heat evolved by the reaction raises the temperature of the water, as indicated on the thermometer B. During the reaction the water is stirred gently with the stirrer C. If, for example, the weight of the water is 800 g and the rise in temperature is 1.5° , the heat evolved is approximately $800 \times 1.5 = 1200$ cal. This estimate of calories is made on the basis that pure water alone is contained in the calorimeter, whereas a *solution* of the reacting substances is really present. A correction must be applied for this, as well as for the heat absorbed by the walls of the Dewar vessel.

Relation of matter and energy. From what has been said about matter and energy it will be seen that we do not have any way of making a fundamental and independent definition of either. We cannot imagine either one without the other, and we are really forced to define each in terms of the other. In fact, it has now been conclusively proved that *under certain extreme conditions matter may be transformed into energy, and possibly energy may be transformed into matter*. It is probable that the intense and appar-

ently inexhaustible radiant energy of the sun is maintained by the slow transformation of its mass into energy. Such transformations are as yet beyond our control, and they do not affect our ordinary experience as expressed in the law of conservation of mass and the law of conservation of energy.

VARIETIES OF MATTER

Compounds, elements, and mixtures. The variety of forms which matter assumes in all the wonderful transformations of nature is almost infinite, and these many forms may be classified in a great many ways, according to the purpose in view. The interest of the chemist centers chiefly in the composition of substances. From this standpoint he classifies substances into three groups, namely, *compounds*, *elements*, and *mixtures*. The distinction can best be explained by some experiments.

Illustrative experiment 1. The chief characteristics of the substances iron and sulfur are familiar to almost everyone. Iron in a finely divided state is a heavy black powder strongly attracted by a magnet. When treated with the liquid known as hydrochloric acid, the iron passes into solution, a colorless gas called hydrogen is evolved, and considerable heat is liberated in the process. Sulfur (as usually obtained) is a light yellow powder not attracted by a magnet nor dissolved by hydrochloric acid. In contrast with iron, sulfur is readily soluble in the liquid known as carbon disulfide; and when the solution is allowed to evaporate, the sulfur is deposited in the form of yellow crystals.

When iron and sulfur are thoroughly ground together, a greenish black powder is obtained which appears to be quite different from either of them; but when we test for the presence of these two materials, we find that in many respects the powder acts like these two taken separately. Carbon disulfide dissolves the sulfur but not the iron. A magnet rubbed through the powder withdraws the iron and leaves the sulfur unchanged. Both the sulfur and the iron act just as they did before they were ground together, and they are said to constitute a *mixture*.

If now a portion of the mixed powder is placed in a test tube and heated, as shown in Fig. 18, it soon begins to glow at the point of greatest heat; and even if the flame is quickly withdrawn, the glow continues to spread throughout the entire contents of the test tube, and a great deal of heat is set free at the same time. When the product is examined, it is found that the characteristics of the iron and sulfur have disappeared. Carbon disulfide no longer dissolves

the sulfur and leaves the iron; a magnet has no effect upon the material; hydrochloric acid dissolves the entire product and evolves

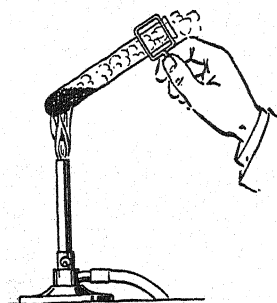


FIG. 18. Heating a Mixture of Iron and Sulfur

a gas of disagreeable odor quite different from hydrogen; the heat liberated by the action of the acid on this material is not the same in quantity as in the case of its action on iron. In fact, this product differs entirely from its constituents in its properties, such as density, color, hardness, solubility, and melting point. This new material is called *iron sulfide*. It is a *compound*, and the chemical change undergone by the two original constituents is described as a *combination*.

Illustrative experiment 2. When a small quantity of sugar is heated in a test tube, it melts, turns brown in color, gives off vapors, and finally dries up to a solid black residue which is easily identified as carbon, or charcoal. By collecting and examining the vapors it is possible to show that they are largely water. To make this transformation of the sugar complete it is necessary to apply heat throughout the entire process. In this experiment one substance, merely by the continued application of heat, has given rise to at least two other substances of very different properties, and the change is described as a *decomposition*.

Chemical reactions. The two experiments that have just been described differ from each other in many ways, but they have several characteristics in common. Most of the properties of the materials concerned undergo a very considerable change, so that it is easy to establish the fact that the products formed are different from the original materials. An equally important characteristic is that the chemical energy of the materials has been changed. The action of iron with sulfur, *when once started*, is attended by the evolution of a great deal of heat, which must come from chemical energy present in the iron and sulfur; that is, the iron sulfide contains less chemical energy than the two original materials.

To effect the decomposition of sugar it is necessary to *supply heat during the entire period of decomposition*. This heat must be converted into some other form of energy. A part of it is converted into chemical energy, so that the carbon and the water taken together possess more energy of this kind than did the original sugar. *Any transformation in matter, whether combination or decomposition, which involves the disappearance of one or more substances and the appearance of one or more other substances possessing properties of their own is*

called a chemical reaction. Accompanying every such reaction is a characteristic energy change.

Chemical compounds. Iron sulfide, described above, belongs to the class of substances known as *chemical compounds*. Since most of the substances with which we shall be concerned are of this class, it is important for us to know the characteristics of the group. In a general way these characteristics are as follows: (1) *A compound is always composed of at least two different substances (elements, p. 27)*; thus iron sulfide is composed of iron and sulfur combined. (2) *The composition of any given compound is always perfectly definite*; thus iron sulfide, no matter how prepared, always contains 63.5 per cent of iron and 36.5 per cent of sulfur. (3) *The chemical energy of a compound is always different from the sum of the chemical energies of its constituents taken separately*. (4) *A compound has its own characteristic properties*, differing from the properties of its constituents; thus iron sulfide possesses properties that are entirely different from those of the iron and sulfur of which it is composed.

Other energy changes that are involved in chemical action. Since in every chemical reaction there is always a change in *chemical energy*, it is evident that *other* forms of energy must also be involved. Usually the loss or gain in chemical energy is indicated by a corresponding evolution or absorption of heat, as shown in the experiments with iron sulfide and sugar. Under the proper conditions the chemical energy may be converted into electrical energy. Thus, if a plate of zinc is connected by a wire with one of carbon, and the two are dipped into hydrochloric acid, the zinc is acted upon by the acid, and at least some of the chemical energy set free appears as an electric current in the wire. In other cases chemical energy is partially converted into light, as when magnesium wire burns, or into kinetic energy, as when the explosion of gunpowder imparts motion to a bullet (Fig. 19).

It is by no means true, however, that a change in energy must necessarily be considered as evidence of chemical action. As we have seen, chemical energy is only one of several forms which may be changed to the familiar forms of heat, electrical energy, and kinetic energy. An energy change in a given case may be due to one or more of many causes other than chemical action. The radiant-energy effect which we observe on turning the key to an electric light may have its source in an electric dynamo driven by a turbine, which in turn may be driven by falling water; and the whole chain of operations may involve no chemical action at all. The heat generated when a gas is compressed represents the mechanical work done upon the gas.

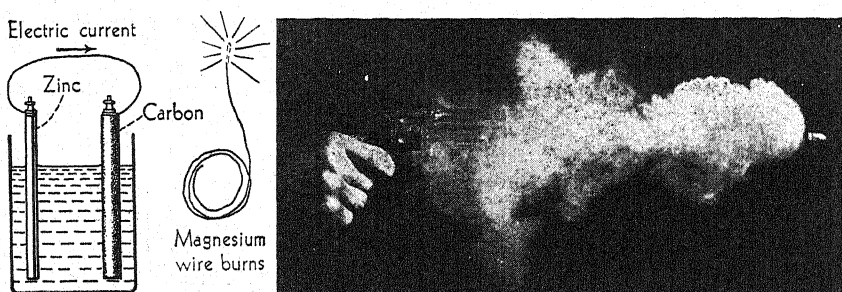


FIG. 19. *Conversion of Chemical Energy into Other Forms of Energy*

H. E. Edgerton

Conditions affecting chemical action. There are many conditions which may either promote or hinder chemical action. An increase in temperature is usually favorable to starting chemical action, as was seen in the case of iron and sulfur. It frequently promotes decomposition, as in the case of sugar. Other factors, such as light, mechanical pressure, shock, and electrical energy, may also facilitate either chemical union or decomposition, in some cases overcoming obstacles which prevent union, in other cases overpowering the chemical affinity which holds a compound together.

Chemical conduct of substances. We have seen that substances are characterized by their physical properties. They are also characterized by the way in which they act toward other substances, as well as by the decompositions (if they are compounds) which they undergo under various conditions. A substance may burn with a flame when heated in the air, or it may combine with another substance with incandescence, as is the case of iron heated with sulfur. It may decompose when heated, as is true of sugar, or when subjected to the action of the electric current, as does water. It may show no action at all with certain substances under ordinary circumstances, while with some of them it may react at high temperatures and with others remain indifferent. All such peculiarities are collectively called the *chemical conduct* (or sometimes the *chemical properties*) of a substance. It will be seen that such conduct usually depends upon the presence of other materials, as well as upon the physical conditions that prevail, such as temperature and pressure.

Elementary substances, or elements. These experiments suggest that it will be of interest to heat iron, sulfur, water, and carbon in turn and see whether any new substance can be obtained through their decompositions; also, to subject them to the action of an electric current or to any other agency that promotes decomposition.

In such ways chemists have succeeded in decomposing water into two invisible gases, oxygen and hydrogen; so that water must be regarded as a compound. On the other hand, carbon, iron, and sulfur, as well as oxygen and hydrogen, have never been decomposed chemically, though many means have been tried. Substances like these five, which resist all ordinary efforts to decompose them, are called *elementary substances*, or *elements*. These elements, about ninety in number, may be regarded as the units, or building materials, out of which every compound is made.

Mixtures and substances.

Many of the materials with which we are most familiar are neither elements nor definite compounds, but *mixtures* of one or both of these. Ordinary concrete is a mixture, for in a broken piece it is easy to identify the fragments of stone, the sand, and the cement binder. Granite is another common mixture, in which individual crystals of mica, feldspar, and quartz may be recognized (Fig. 20). Mixtures differ from elements and compounds in that they are not of even quality throughout; that is, mixtures are not *homogeneous*. Despite the apparent uniform character of many fine-grained mixtures, such as that of iron and sulfur, an examination under the microscope shows that the uniformity is not real; for, in the magnified image, the particles of iron and sulfur can be seen lying side by side unchanged. The term *substance* and also the term *material* are commonly applied alike to elements, compounds, and mixtures. The term *pure substance* is reserved for elements and compounds, since the word *pure* excludes mixtures.

In many cases mixtures and compounds resemble each other very closely, and it sometimes becomes difficult to distinguish them. For



FIG. 20. A Picture of Granite

Spencer

example, alcohol and water mix in all proportions to form a perfectly homogeneous liquid; and copper and zinc when melted together form brass, which in properties is quite different from both original metals. However, in neither of these two cases is the heat given off during the mixing nearly as great as we should expect in a typical chemical reaction; and furthermore, neither mixture has a fixed percentage composition. These two illustrations are examples of a fourth class of substances, called *solutions* — the one a liquid solution and the other a solid solution. Solutions will be discussed at length in a later chapter.

ARITHMETIC AND CHEMISTRY

Ratio and proportion. As we have already suggested, many of the important relationships and much of the beautiful logic of chemistry come to light only after quantitative treatment of observations. Any quantitative study involves an attempt to establish number relationships and calls for the use of arithmetic. The arithmetic which we shall use in this text is very simple and will generally test the student's power to calculate with nothing more difficult than the simple mathematical tools of *ratio* and *proportion*.

The technique of ratio and proportion is especially useful whenever, in our thinking, we have to do with change of scale. For example, suppose that we are looking at the floor plans that are to be followed exactly in the construction of a house. We can be sure that the floor space A in the dining-room of the completed house will be related to the floor space B of the final living-room in just the same way as the floor space a of the dining-room is related to the floor space b of the living-room on the much smaller-scaled blueprint. In making this statement we have set up two ratios and a proportion. We have said that A is to B as a is to b . This may be stated, $A : B = a : b$. Here $A : B$ is a *ratio*, and so is $a : b$. The equation in which the two ratios are set down as being equal is a *proportion*.

We may say this in other ways, all of which are equivalent :

$$A \div B = a \div b, \text{ or } \frac{A}{B} = \frac{a}{b}$$

Note that no statement is made that $A = a$ or that $B = b$. It is the *ratio* $\frac{A}{B}$ which is equal to the *ratio* $\frac{a}{b}$. Of course, if $\frac{A}{B} = \frac{a}{b}$, it follows that $\frac{B}{A} = \frac{b}{a}$; also that $\frac{A}{a} = \frac{B}{b}$, and that $\frac{a}{A} = \frac{b}{B}$.

The thing about a proportion that makes it helpful is the fact that if three of the four terms are known, the fourth can always be calculated. Let us illustrate. Suppose that we should like to calculate the height of

the Washington Monument. We can do so by using a proportion, if we measure the length of the monument's shadow (Fig. 21) and at the same time set up a vertical rod of known height and measure the length of its shadow. The statement of the proportion would be

$$\frac{h}{s} = \frac{H}{S} \quad H = ?$$

Since S , h , and s are all known, the equation may be solved for H ; that is $H = \frac{Sh}{s}$. In a proportion, generally one of the ratios is known, and only one term of the other ratio is known. We may call the *known* ratio the *pilot* ratio, since it guides us to a solution for the unknown term in the other ratio. In the case above, the ratio $\frac{h}{s}$ is the pilot ratio.

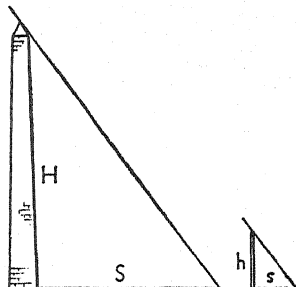


FIG. 21. Diagram Illustrating the Calculation of Heights by Proportion

Chemists' use of proportion. Chemists are very deeply and intimately concerned with questions calling for a change of scale. If we do a certain thing on a certain scale with a certain result, what will happen if we do it on a different scale? If 1 teaspoonful of sugar is needed to sweeten 1 glass of lemonade, how many teaspoonfuls are needed for 100 glasses of lemonade? The answer is obviously 100; but the answer comes from the solution of the proportion $1 : 1 = x : 100$. Or, take the following illustration: If 55.85 g of iron react with 32.06 g of sulfur, how many grams of sulfur are needed to react with 1000 g of iron? The proportion is

$$\begin{array}{ccccccc} & \text{pilot ratio} & & & & & \\ 55.85 \text{ g} : 32.06 \text{ g} & = & 1000 \text{ g} : x \text{ g} \\ \text{iron} & \text{sulfur} & \text{iron} & \text{sulfur} & & & \\ 55.85 \times x & = & 32.06 \times 1000 \\ \text{Ans. } x & = & 574.1 \text{ g of sulfur} \end{array}$$

How many tons of iron will react with 2 tons of sulfur? The proportion is

$$\begin{array}{ccccccc} & \text{pilot ratio} & & & & & \\ 55.85 \text{ g} : 32.06 \text{ g} & = & x \text{ tons} : 2 \text{ tons} \\ 32.06 \times x & = & 2 \times 55.85 \\ \text{Ans. } x & = & 3.48 \text{ tons of iron} \end{array}$$

Many of the chapters of this book will be concerned with questions and problems, in great variety, and in many different kinds of settings, which will call for solution by the use of proportions. It is extremely important that the student learn to set up a simple proportion and to solve for the unknown term.

Exponential arithmetic. 1. *Large numbers.* Not infrequently chemists must use very large numbers in their calculations. For instance, the number

of molecules in a cubic centimeter of air is about 27,000,000,000,000,000. We may avoid the labor of writing so many ciphers and express such numbers much more conveniently and compactly in terms of exponents of 10. Thus the number just given, 27 quintillion, may be written as 27×10^{18} , where the *exponent* of 10 indicates the number of ciphers to be added to the 27. Or it may preferably be written as 2.7×10^{19} . To show more fully how this system is employed in writing numbers, the following table is given:

$1 = 10^0$	$5 = 5 \times 10^0$
$10 = 10^1$	$50 = 5 \times 10^1$
$100 = 10^2$	$500 = 5 \times 10^2$
$100,000 = 10^5$	$537,000 = 5.37 \times 10^5$
$100,000,000 = 10^8$	$128,000,000 = 1.28 \times 10^8$
$1,000,000,000 = 10^9$	$1,280,000,000 = 1.28 \times 10^9$

2. Small numbers. Similarly the very small numbers which are often used in chemical calculations may be expressed in terms of the *negative* exponents of 10. A table will help to make the method clear.

$0.1 = \frac{1}{10} = \frac{1}{10^1} = 10^{-1}$	$0.5 = 5 \times 10^{-1}$
$0.01 = \frac{1}{100} = \frac{1}{10^2} = 10^{-2}$	$0.053 = 5.3 \times 10^{-2}$
	$0.000013 = 1.3 \times 10^{-5}$
	$0.0000008 = 8 \times 10^{-7}$
$0.0000001 = \frac{1}{10,000,000} = \frac{1}{10^7} = 10^{-7}$	

As a further example, a piece of gold, just too small to be visible in the most powerful microscope, weighs about 0.000,000,000,000,019 g, or, expressed in the exponential system, 19×10^{-15} g, or 1.9×10^{-14} g.

3. Calculations. As far as additions and subtractions are concerned, the exponential arithmetic offers no particular advantage; but it is especially helpful and convenient in performing the multiplication and division of large and small numbers. For example, suppose we wish to multiply 32,100,000,000,000 by 3,000,000. We may write the two numbers as 3.21×10^{13} and 3×10^6 . The 3.21 and 3 are multiplied together, and the *exponents* are added. The product is 9.63×10^{19} . If we multiply 3.21×10^{13} by 3×10^{-6} , the result is 9.63×10^7 .

$$\begin{array}{r} 3.21 \times 10^{13} \\ 3 \times 10^6 \\ \hline 9.63 \times 10^{19} \end{array}$$

$$\begin{array}{r} 3.21 \times 10^{13} \\ 3 \times 10^{-6} \\ \hline 9.63 \times 10^7 \end{array}$$

If we wish to divide 3.21×10^{13} by 3×10^6 , the number 3.21 is divided by 3, and the exponent 6 is subtracted from the exponent 13. The quotient is 1.07×10^7 . To divide 3.21×10^{13} by 3×10^{-6} , the number 3.21 is again divided by 3 and the exponent -6 is subtracted from the exponent 13. The result is 1.07×10^{19} .

$$\frac{3.21 \times 10^{13}}{3 \times 10^6} = 1.07 \times 10^7$$

$$\frac{3.21 \times 10^{13}}{3 \times 10^{-6}} = 1.07 \times 10^{19}$$

With a little practice the student can easily acquire considerable skill with exponential arithmetic and save himself a great deal of time and labor.

Questions

1. How could the weight of a cannon ball be changed without changing its mass? Could its mass be changed without changing its weight?

2. Name all the transformations of energy which are involved in the following processes: (a) the explosion of dynamite; (b) the motion of a coal-fired locomotive along a track; (c) the running of a watch; (d) the operation of a lighting system from a storage battery which is charged by a dynamo driven by a steam engine; (e) the pumping of water (into a storage tank) by a windmill.

3. Reconcile the following facts with the law of conservation of mass: (a) a piece of sulfur burns and disappears entirely; (b) a lump of coke burns, and the ashes weigh less than the original coke; (c) a piece of iron burns, and the resulting product weighs more than the iron.

4. Refer to the table giving the "Densities and Melting Points of Some of the Elements," in the Appendix. (a) Which of these elements has the least density and which the greatest? (b) Which one has the highest melting point and which the lowest? (c) Name those that are liquid at ordinary temperatures. (d) Name those which are still solid at 2000°.

5. Give examples of changes that involve (a) no change in composition; (b) a change in composition.

6. Define *element*, *compound*, and *mixture*.

Problems

1. At a certain temperature, well below the freezing point of water, the scale readings of a centigrade and Fahrenheit thermometer are the same. What is this temperature?

2. A sample of anthracite, weighing 1.25 g, was burned in a calorimeter containing 2500 g of water. The heat evolved by the burning of the coal raised the temperature of the water from 15° to 18.7°. (a) Calculate the number of calories of heat evolved per gram of coal. (b) To how many joules would this be equivalent?

3. How many volt-coulombs of electrical energy would be required to heat 3000 g of water from 20° to 95° with an electric heater immersed in the water in a thermos bottle?

4. Refer to the table of densities in the Appendix and (a) calculate the volume (cc) of a diamond weighing 2.58 g. (b) What is its volume in cubic millimeters? (c) A cube of aluminum weighs 21.616 g; what is the length (cm) of the cube edge? (d) How many grams would a cube of gold of the same size weigh?

5. (a) Calculate the weight in milligrams of a silver bullet (sphere) 6 mm in diameter. (b) How many such bullets, to the nearest whole number, could be made from 1 oz of silver?

6. Perform the following operations: (a) $(1.24 \times 10^4) + (26.3 \times 10^3)$; (b) $(4.8 \times 10^6) \div (2 \times 10^2)$; (c) $(5.5 \times 10^{-5}) \times (11 \times 10^{-3})$; (d) $(6.4 \times 10^7) \times (2.2 \times 10^{-4})$; (e) $(1.62 \times 10^{-3}) \div (81 \times 10^2)$.

7. If sunlight on the average delivers 2 cal/min/cm² of surface on which it falls, how much heat would be received by 1 acre of ground in 1 hour?

8. (a) If water is flowing from a faucet at the rate of 1 g/sec into a tray 1 m² in area, to what depth will the tray be filled in 5000 sec? (b) If the tray of water is then placed in average sunlight for 5 min, what will be the rise in temperature of the water (assume no loss of heat)? (See preceding problem.)

9. (a) If 55.85 g of iron react completely with 32.06 g of sulfur to form iron sulfide, what weight of the latter is produced? (b) If the total quantity of iron produced in this country annually, say 50 million tons, were converted to iron sulfide, what tonnage of sulfur would be required?

Reading References

FOSTER. *The Romance of Chemistry*. Chapter II, entitled "Things Seen and Unseen: The Tangible and the Intangible," deals with matter and energy. Chapter IV deals with chemical elements and compounds.

HAUBEN. "The Derivation of the Names of the Elements," *Journal of Chemical Education*, Vol. X, pp. 227-234.

WEEKS. *The Discovery of the Elements*. Chapter I, "Elements Known to the Ancient World," and Chapter II, "Elements Known to the Alchemists," tell an interesting story about early knowledge regarding the elements.

The magazine *Fortune*, Vol. XVIII, No. 5, pp. 85 ff., treats of "The Sources of Energy."

CHAPTER 3

Particles of Matter

The particle nature of matter. The idea that *all matter is made up of particles* (very small, invisible particles) is not at all a new idea. The written records show that some of the early Greek philosophers used the idea in their speculations. Possibly it is much older than the Greeks. During the nineteenth century the conception of the particle structure of matter played a most important role in the thinking of chemists and physicists; and it passed, during the course of the century, through the various stages of plausibility from hypothesis to theory, and finally, today, it may be said to have attained the status of accepted fact. Most modern chemists feel that we probably have just as good reason for believing in the objective reality of these invisible particles of matter as we have for believing in the actual existence of matter itself — for example, in the existence of the pages of this book.

At any rate, the idea that all matter is made up of particles is the fundamental basis of modern chemical theory. We set up our explanations of the behavior of matter, in all its myriad forms, in terms of the weight, size, shape, and structure of these particles, and in terms of their motions, their mutual attractions and repulsions, their collisions and combinations with one another.

Since the particles to which we are now referring are so extremely small that they cannot be seen even with the most powerful microscope, one naturally wonders how we can be so sure that there really are such particles. Let us now consider a few of the arguments.

1. *Evaporation and diffusion.* If a piece of camphor is placed in a large room of quiet air, the odor of camphor can very quickly be perceived everywhere in the room. The piece of camphor will itself eventually disappear. It would be exceedingly difficult, if not impossible, for us to explain satisfactorily how the evaporation of the camphor and its diffusion throughout the room could occur on any other basis than that it is simply a case of the disengagement of invisibly small *particles* of camphor from the piece of camphor and their spread in all directions through the air. How could the piece of camphor possibly disappear without our seeing it go unless tiny invisible particles of it are escaping? And how could the camphor spread out into the relatively enormous volume of a room unless

there are little particles of it that separate from one another and scatter through the air of the room?

2. *Solution and diffusion.* If we drop a few crystals of a colored dye, such as methyl violet, into a beaker of water (A in Fig. 22), the

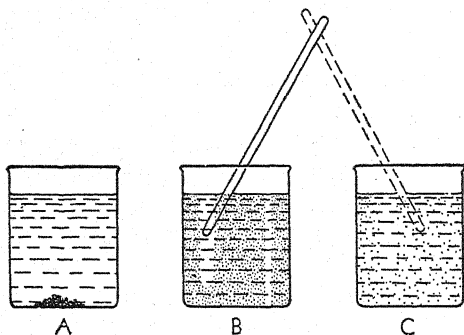


FIG. 22. *Solution and Diffusion*

crystals dissolve and soon a deep violet color spreads throughout the entire volume of water (B). If we dip a glass tube into this and transfer a few drops of the colored solution to another beaker of fresh water (C), the color spreads again, although its intensity is now much less. Our explanation of these effects is that the crystals of methyl violet are made up of *particles* of methyl violet. These *particles* themselves have a violet color. The "dissolving" of the crystals is the breaking away of the *particles*, which then move off into the water. The deep color of the solution in beaker B is to be attributed to the enormous number of *particles*, billions of billions of them, spread out through the volume. If a relatively small portion of this large number of *particles* is dipped up and dropped into the volume of water in beaker C, the resulting more dilute solution will naturally possess less color than the more crowded system of *particles* in beaker B. It is indeed difficult to conceive how any other explanation of the observed facts is possible.

3. *The radiometer.* Everyone who has looked into a jeweler's shopwindow has seen a radiometer, with its vanes spinning around in the sunlight. The explanation of this effect takes us back to an experiment performed by Benjamin Franklin when he was living in Philadelphia. One morning after a fresh fall of snow, when the warm sunlight was beginning to melt the snow, Franklin went into his back yard and spread out two pieces of cloth, one black and the other white. He observed that the snow melted much more rapidly under the black cloth and concluded that a black surface absorbs sunlight more readily than a similar white surface. The same principle is involved in our choice of white or light-colored clothes for wear in hot summer weather and in the tropics, rather than black or dark clothes.

A Crookes radiometer (Fig. 23) consists of a small spindle which carries four vanes, placed 90° apart, and mounted so that the whole

will spin (like a top) in a glass bulb from which most but not all of the air has been pumped out. Every vane is polished on one side and blackened with lampblack on the other. When sunlight or any strong light shines on the vanes, the black sides absorb the light better and become appreciably warmer than the polished sides, which reflect the light. When the *particles* of air which are moving about quite freely in the partially evacuated glass bulb strike the warmer side of the vane, they acquire a greater velocity of motion and bounce away more violently than from the polished side.

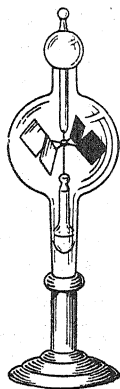


FIG. 23. A Crookes Radiometer

The effect is somewhat like that of shooting a gun : the bullet goes one way and the butt of the gun recoils and strikes one's shoulder ; the particles of air jump away from the lampblackened vane, and the vane goes the other way. The recoil is sufficient to make the imagine how the spinning of the radiometer vanes could be induced without the *particles* of air.

4. The Brownian motion. Through a microscope of medium power it is easy to see fine dust floating in quiet air or, better still, the minute droplets of which tobacco smoke consists (Fig. 24). We notice that the droplets are dancing about, back and forth, up and down, in and out, with a restless haphazard sort of motion. This motion, named for an English botanist Brown who discovered it about one hundred and twenty-five years ago, can be explained satisfactorily only by assuming that the suspending medium (in this case, air) in which the droplets are floating is made up of *particles*. These *particles* are themselves possessed of random motion by virtue of their temperature energy, and they continually bump into the floating droplets and jostle them about. One cannot see the *particles of air*, but one can see the direct effects of their impacts on the droplets.

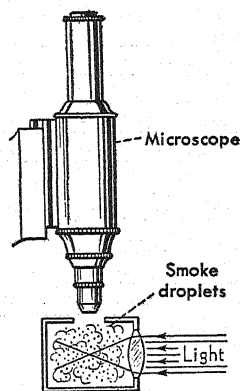


FIG. 24. Arrangement for Observing Brownian Motion

This observed Brownian motion is very convincing evidence for the existence of *particles* of matter ; it is one of the classic arguments. Every student should avail himself of the opportunity of seeing this impressive spectacle.

5. *The spinthariscopes*. A zinc sulfide screen, over which are mounted a bit of radium and a lens, is a little device known as a *spinthariscopes* (Fig. 25). The name means an instrument for seeing scintillations, or glints of light. If the screen is observed in a dark room, it appears to glow, like a radium-treated watch dial. If one looks at the glow through the magnifying lens, one sees millions of tiny, individual flashes of light. Every flash is produced by the impact on the screen of a *particle* (the so-called alpha particle) shot off during the disintegration of the radium. This alpha particle is an atom of helium having an electric charge. Seeing the separate flashes produced by the impact of individual atoms is almost as good as seeing the atoms themselves. Indeed, as we shall show a little later, a modified spinthariscopes has *actually been used to count atoms*.

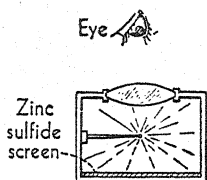


FIG. 25. *Spinthariscopes*

The foregoing arguments are of two different kinds. In the case of the first four effects, (1) evaporation and diffusion, (2) solution and diffusion, (3) the radiometer, and (4) the Brownian motion, we are in every case convinced of the existence of particles of matter because it seems impossible to explain the effect — that is, to find the cause for the effect — except in terms of *crowds* of particles. In the case of (5), the spinthariscopes, the force of the argument is even more overwhelming, since we observe the direct effects of what must certainly be separate, *single* particles striking the zinc sulfide screen. There are many other arguments, of the first kind and of the second kind, which could be given; and some of these will be alluded to in later chapters.

Nature of the particles. It is not very difficult to find evidence for the existence of particles of matter. But, after we know that they exist, to discover the details of the nature of these invisible particles, their weight, size, shape, structure, etc., is naturally a much more difficult problem.

In the following sections of this chapter, on ATOMS, IONS, and MOLECULES, we shall describe some of the things which have been discovered about the nature of these particles without, in many cases, telling how such conclusions have been reached. It is well to present this preliminary survey now, not only for the sake of defining certain terms and introducing the common symbols which chemists use, but also to make our task of actual explanation, later on, much easier and simpler.

ATOMS

The atom the ultimate particle of an element. Among the various kinds of particles the first that we shall discuss will be the *atoms*. We have already referred, in Chapter 2, to the ninety or more elements of the chemist, such substances as aluminum, carbon, chlorine, copper, helium, hydrogen, iron, mercury, nitrogen, oxygen, silver, sodium, and sulfur. Most of us already have a reasonably good knowledge of the appearance and general physical properties of some of the more common elements. We shall describe the chemical and physical properties of the important elements in the technical language of the chemist at the proper places, later. At present the points that we wish to make are (1) that whenever we deal with these elementary substances or handle them, we handle pieces or lumps or certain quantities of them; (2) that such pieces or quantities of the elements are made up of extremely small particles. *These ultimate particles of the elements are called atoms.*

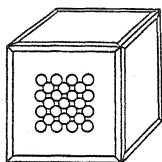


FIG. 26. *Diagram Showing Arrangement of Atoms in a Crystal of Copper*

Let us illustrate what we mean by taking a small crystal of the element copper. Such a piece of copper is made up of many, billions of billions of atoms of copper. By a method which will be described in Chapter 5, it has been shown that the invisible atoms in the crystal of copper are arranged in the definite pattern indicated in Fig. 26. Of course the question of whether or not the atoms are arranged in any special way is beside the point, at the moment, since what we wish to emphasize is that any quantity of any element which can be handled is made up of a vast number of atoms, in the same sense that a bucket of sand is made up of a great many grains of sand.

Resemblances and differences among atoms. In some respects the atoms of the different elements resemble one another. For example, all the atoms of all the elements probably have approximately the same *shape*. They are probably little spheres, or nearly spherical in symmetry. Also all the atoms of the different elements have essentially the same *type of structure*, namely, a nucleus, which carries a positive electric charge, at the atom's center, around which circulate negatively charged particles called *electrons* (in somewhat the same way that the planets revolve around the sun) (Fig. 27).

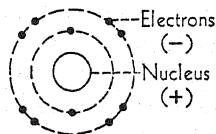


FIG. 27. *Diagram Showing the General Structure of an Atom*

On the other hand, there are differences. The atom of any one element differs from the atoms of other elements in *size* and also in average *weight*. While all the atoms have nuclei and circulating electrons, the details of structure are quite different for atoms of different elements. Different atoms show different *chemical behavior*. All these things will be discussed eventually at great length, and our statements here will be qualified to a slight extent.

Union of atoms. The atoms of some of the elements can attach themselves to other atoms. Long ago chemists symbolized such a



FIG. 28

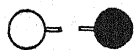


FIG. 29

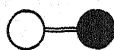


FIG. 30

*Ways of Sym-
bolizing the
Union of Atoms*

union by the engagement of little hooks which the atoms were supposed to possess (Fig. 28). Modern chemists leave off the hooks and indicate the union by drawing two half-bonds pointing toward one another (Fig. 29), or more usually by drawing a dash line, —, or *bond*, between the two atoms (Fig. 30). Nevertheless, when chemists use the dash-line bond, there is always the implied understanding that each of the two atoms *contributes its share of the bond*, just as though there were a hook on each atom, or just as though each atom had a hand which could reach out and clasp the hand of the other atom.

Meaning of the bond. When a chemist draws a bond, he does not mean to imply that there is an *actual* tiny rod or stick connecting the atoms. He does not mean to imply anything about the exact mechanism by which the atoms are held together. Whatever the nature of the actual bond may be, there is no doubt that there is a union of atoms. This is the sense in which the symbol is used, to indicate the fact of union (and also that each atom does its share).

Theory of the bond mechanism. As a matter of fact, however, chemists feel that they now have a reasonable picture, perhaps something close to the true picture, of what a chemical bond is. Fig. 31 represents, in a highly diagrammatic way, the bonding together of the two atoms A and B. Each atom has a nucleus at its center, and, in this case, each atom has a single electron. Each atom gives its electron to form a *pair of electrons*, and the two electrons of the pair probably spend most of their time between the two nuclei, as shown in the figure. The electrons probably also circulate around *both* nuclei, some of the time. The nuclei are positively charged and the electrons negatively charged. These op-

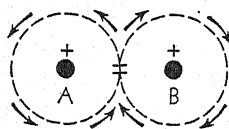


FIG. 31. *Diagram Illustrating the Theory of Chemical Bonds*

posite charges attract one another. The presence of the negatively charged electrons *between* the two positively charged nuclei helps to bind the atoms together. This type of bond is known as a *covalent* bond (see Chapter 14).

Symbols for the atoms. At one time chemists used various hieroglyphic symbols for the atoms of the elements or for the elements. For instance, such symbols as the following were in vogue: \odot for gold, \wp for copper, ♂ for iron, C for silver, and ☿ for mercury. These symbols seem a little cumbersome to us now, and too much like Chinese writing. The easiest thing for us to do, and the thing that modern chemists do, is to abbreviate the name of the element with a single capital letter or with two letters, and let this abbreviation be the symbol for the atom of that element. Thus H is the symbol of the atom of hydrogen, and O that of oxygen. Because several names begin with the same letter, it is often necessary to add a second letter to the first. Thus C stands for the atom of carbon, Cl for that of chlorine, and Ca for that of calcium. In some cases a symbol is an abbreviation of an old Latin name of the element. In this way Fe stands for the atom of iron (*ferrum*), Cu for that of copper (*cuprum*), and Hg for that of mercury (*hydrargyrum*).

When chemists wish to refer to an *element*, they use the full name of that element, and not the abbreviation. For example, a chemist does not say, "This sealed flask contains He." What he says is "This sealed flask contains helium." As with the names of other elements, the word *helium* refers to the *substance* itself, regardless of quantity. The quantity may be large or small; *helium* may refer even to a single atom. But the symbol He is reserved for use when one expressly wishes to refer to an *atom* of helium. It is true that the atomic symbol is *also* used to denote a very special number of the atoms of the element (see Chapter 4).

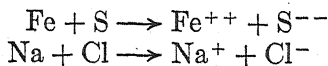
IONS

Ions are electrically charged particles. Another extremely important kind of particle with which chemists are concerned is the *ion*. It turns out that electricity itself consists of *particles*, or units, of electricity. These are of two kinds, — positive and negative, — and each positive particle exactly balances a negative particle. As we have seen, the positive particles are lodged in the nucleus of the atom, while the negative particles (the *electrons*) circulate around the positive nucleus. In normal atoms the sum of the positive charges on the nucleus just balances the sum of the negative electrons.

Under some conditions an atom may lose one or more of its electrons, which leaves the (modified) atom positively charged by one or more units of electricity. Other atoms may capture one or more extra electrons and are then negatively charged. *These modified atoms, electrically charged, are called ions*, and the original atoms giving rise to them are said to be *ionized*.

Ions of metals. Usually the atoms of the *metals*, like sodium, potassium, calcium, zinc, or aluminum, when they become ions, carry a *positive* charge. The symbols for the atoms of these particular metals are Na, K, Ca, Zn, Al; and the symbols for their ions are Na^+ , K^+ , Ca^{++} , Zn^{++} , Al^{+++} . When ionized, some atoms lose only one electron, others two, and some three, but seldom more than three. Certain atoms may lose different numbers of electrons under different conditions. Thus, the ions of copper are Cu^+ and Cu^{++} , of iron Fe^{++} and Fe^{+++} , of gold Au^+ and Au^{+++} .

Ions of nonmetals. On the other hand, the atoms of the nonmetals, such as chlorine, bromine, oxygen, and sulfur (Cl, Br, O, S), tend to acquire extra electrons, to give the ions Cl^- , Br^- , O^{--} , S^{--} . Many chemical reactions involve the transfer of one or more electrons from a metal atom to a nonmetal atom to form ions. Such reactions may be represented by symbols, with an arrow drawn to show the course of the electron transfer, thus:



Attraction between ions. Once such ions are formed, they are quite stable and ordinarily do not easily become neutral atoms again. The positive and negative ions exist side by side and attract one another strongly, just as two oppositely charged pith balls (Fig. 32) attract each other. The ions do not usually aggregate in pairs, however, but in much larger clusters, with the various ions surrounded by several ions of opposite charge, and all arranged in an ordered pile. For example, a crystal of common salt, sodium chloride, is made up of sodium ions (Na^+) and chlorine ions (Cl^-) bound together by electrostatic attraction in a regular array like a three-dimensional checkerboard (Fig. 33). There are just as many sodium ions as chlorine ions in this crystal; and while actually every Na^+ is surrounded by six Cl^- (above, below, front, back, right, left), and every Cl^- is surrounded by six Na^+ , we can think of them all as being balanced in pairs (Na^+ , Cl^-) for the sake of indicating that the number of positive charges and the number of negative charges are equal.

Most atoms in our earth's crust exist, as a matter of fact, not as neutral atoms but as *ions* (simple or complex), and have been ions for

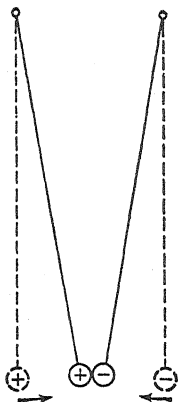


FIG. 32. *Oppositely Charged Pith Balls Attract Each Other*

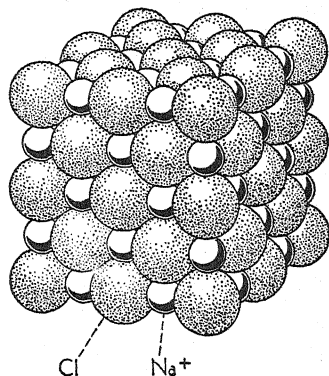


FIG. 33. *Arrangement of Ions in a Crystal of Sodium Chloride*

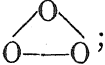
many hundreds of millions of years — probably since the time our earth was formed. The vast masses of igneous and sedimentary rocks and crystalline minerals are ordered piles (or lattices) of positive and negative ions. Attention is being called to these matters at this time so that we may realize how very abundant and common the ions are. For instance, very few of the metals, and very little of these few, are found free in the earth's crust. When we wish to obtain metals, such as iron, lead, aluminum, and zinc, it is the metallurgist's task to change the ions of these metals, as found in minerals, into neutral atoms by suitable metallurgical processes.

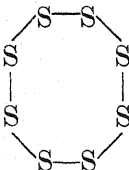
MOLECULES

Molecules are groups of atoms. Still another most important kind of particle, out of which many forms of matter are made, is the *molecule*. Chemists have sometimes used this term in a very broad sense for *any* kind of particle, even including the single atom. But as the word is ordinarily used, *molecule* means a group or cluster of atoms held firmly together by some type of chemical bonding. We recognize three different general kinds of molecules.

1. **Molecule of an element.** Two single atoms of an element, in certain cases, can become fastened to one another by a chemical

bond to form a molecule, or cluster, containing two atoms, thus: $\bullet-\bullet$. This might be called a twin-atom molecule. Some of the elements whose atoms behave in this manner are hydrogen, oxygen, nitrogen, chlorine, bromine, and iodine. Using symbols for the atoms we can indicate the structure of these molecules: $\text{H}-\text{H}$, $\text{O}=\text{O}$, $\text{N}\equiv\text{N}$, $\text{Cl}-\text{Cl}$, $\text{Br}-\text{Br}$, and $\text{I}-\text{I}$. The atoms of the element oxygen

will also form a triplet-atom molecule, ozone, possibly ; phosphorus, a quadruplet-atom molecule, $\text{P}=\text{P}$; and sulfur an

octuplet-atom molecule, . All these molecules can be

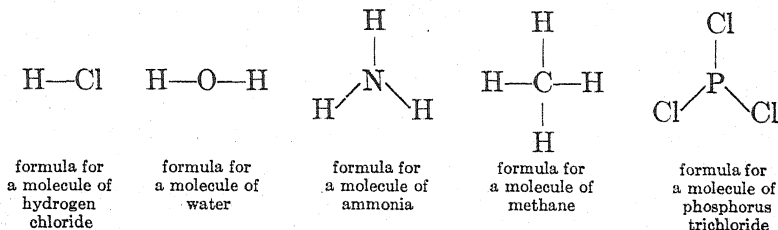
broken down, by suitable means, into single atoms.

Formulas. Such sets, or clusters, of symbols, which we have just employed to represent the known structure of a molecule, are called *formulas*; and the particular ones just given are *structural formulas*, since they show, by the manner in which the symbols are joined together in each formula, the actual manner in which the atoms are connected one to another in the molecule. In the type of formula known as a *molecular formula* no attempt is made to indicate which atoms are connected; but merely the *number* and *kind* of atoms are shown. The molecular formulas for the foregoing molecules are H_2 , O_2 , N_2 , Cl_2 , Br_2 , I_2 , O_3 , P_4 , S_8 . The number following the symbol gives the number of atoms present in the molecule. French chemists write these numbers as superscripts (H^2 , O^2 , P^4 , S^8), but American, British, and German chemists write them as subscripts.

2. Molecule of a covalent compound. The molecule of the type which we have just been discussing is, as we have already said, a molecule of an *element*, since the molecule contains atoms of only one kind. Such molecules are not molecules, or particles, of a compound, though it is true that the atoms within the molecule are "combined" with one another, in the sense of being held together by chemical bonds. In Chapter 2 one of the characteristics of a compound was stated as follows: *A compound is always composed of at least two different elements*. Bearing this in mind, we may now go on to say that there is another type of molecule (again a cluster of atoms), containing *at least two* different kinds of atoms, that such molecules are the ultimate particles of *compounds*, and that the

quantities of compounds which we can handle are made up of vast numbers of these molecules in the same sense, again, in which a bucket of sand is made up of many grains of sand.

The following formulas show the structure of some typical covalent molecules:



It will be noted that every one of these five molecules is composed of two different kinds of atoms. Later in this book we shall have occasion to discuss more complicated molecules made up of three, four, or more different kinds of atoms.

The formulas given are *structural formulas*, since they show which atoms are joined. The corresponding *molecular formulas* would be HCl (or ClH), H_2O (or OH_2), NH_3 , CH_4 , PCl_3 . Again the subscript after the symbol for the atom indicates the number of that particular kind of atom in the molecule. (The Frenchman would write these formulas, ClH , H_2O , NH^3 , CH^4 , PCl^3 .) If there is one atom of a given kind present in the molecule, and only one of this kind, then in the formula the subscript number 1 is understood and is omitted; that is, one does not write N_1H_3 and C_1H_4 , but merely NH_3 and CH_4 .

Valence. In these molecules the H atoms and Cl atoms are connected by only *one* bond; the O atom carries *two* bonds, the N and P atoms *three*, and the C atom *four*. Chemists employ the term *valence* to indicate *the number of bonds which an atom possesses*. In these particular molecules the valence of H and of Cl (hydrogen and chlorine atoms) is 1, of O is 2, of N is 3, of P is 3, and of C is 4. These compounds are called *covalent* compounds, and the bonds (or valences) holding the molecule together are *covalent* bonds (p. 39).

3. Molecule of an electrovalent compound. The ions in the ordered pile of a crystal lattice — for example, Na^+ and Cl^- in a crystal of sodium chloride — are also bound together by chemical bonds, although the bonds are different from covalent bonds. This other type is known as an *electrovalent bond*. It binds *ions* (*oppositely*

charged atoms) together by electrostatic attraction. Such ionic compounds are called *electrovalent* compounds.

Since such an ordered pile of ions is a cluster, there is no reason why chemists should not call the whole crystal of sodium chloride a *molecule*; and as a matter of fact, some chemists do apply the term *molecule* to ion crystals. To do this is a little awkward, however, and would sometimes get us into serious difficulties. For instance, sodium chloride crystals of various sizes from the smallest to the largest would all be "molecules," and the term would thus have a rather indefinite meaning. Also, if we wished to write the *formula* for a crystal molecule of sodium chloride, we should have to indicate in the formula the numbers of Na^+ and Cl^- in the crystal, whatever its size might be. Even in the smallest crystals with which we deal there are many billions of billions of ions. We might write such a formula as $(\text{Na}_x^+, \text{Cl}_x^-)$, where x is an *extremely* large number (and of course it would have to be the right number to fit the particular case).

Before 1914 chemists did not know that crystals of the compounds which today we call electrovalent compounds are actually made up of ions. They thought that crystals of sodium chloride were built of covalent molecules, the formula for which they wrote as $\text{Na}-\text{Cl}$ (or molecular formula NaCl). Even today, about twenty-five years after this old theory was shown to be incorrect, most chemists still write the formula for sodium chloride as NaCl , for calcium chloride as CaCl_2 , and for iron sulfide as FeS . The important thing indicated by these formulas is the *number ratio* between the two kinds of atoms of the compound, and for most practical purposes this is what the chemist wants to know. When it became evident that the formulas should be $(\text{Na}^+, \text{Cl}^-)$ and $(\text{Ca}^{++}, 2 \text{Cl}^-)$, the *number ratio* was not changed, but only our concept of the nature of the forces holding the ions in the crystals in their definite ratios. Since the ions are merely charged atoms of almost exactly the weight of the atoms from which they are formed, the formulas NaCl and $(\text{Na}^+, \text{Cl}^-)$ mean the same thing by weight, the same thing in *number ratio*, and a different thing in the *nature of the bonds* holding the atoms together. We define the molecule of an electrovalent compound as *the smallest set of positive and negative ions which gives the ratio in which they are found throughout the crystal*. Thus, we set up a definition of an electrovalent molecule which makes the molecule independent of the size of the crystal and independent of the particular geometrical pattern in which the ions may be arranged in the ordered pile.

Valence of ions. *The number of charges on an ion is its valence.* The valence of H^+ is 1, of Na^+ is 1, of Ca^{++} is 2, and of Al^{+++} is 3; and the valence of Cl^- is 1, of O^{--} is 2, and of S^{--} is 2. We must remember that these single charges of opposite *sign*, + and -, are always of the same *size*; one just balances, or neutralizes, the other. Any crystal of an electrovalent compound is neutral over all; so the total number of + charges just balances the total number of - charges, and the smallest set of ions (the molecule) will also be neutral. The formula for the molecule will show the same number of + charges as of - charges. The formula for a molecule of sodium chloride is (Na^+, Cl^-) , for calcium chloride it is $(Ca^{++}, 2 Cl^-)$, for aluminum chloride it is $(Al^{+++}, 3 Cl^-)$, for lime it is (Ca^{++}, O^{--}) , for iron sulfide it is (Fe^{++}, S^{--}) , and for sodium oxide it is $(2 Na^+, O^{--})$.

ATOMIC WEIGHTS

Introduction. So far in the statements which we have been making about the theory of the nature and behavior of the common particles, — the atoms, the ions, and the molecules (without having as yet justified our statements), — we have been largely concerned with the definition of terms and with a brief discussion of the meaning of certain names and symbols which chemists apply to these particles. Now we are ready to show how it is possible to find the *weights* of the atoms, or rather their *relative weights*, called their *atomic weights*. Probably nothing is more important to chemists than to know the relative weights of the atoms.

Weighing the atoms. One cannot, of course, weigh a single atom. It not only is far too small to be weighed, but also is much too small even to be seen. Nevertheless it is possible to calculate the relative weights of the atoms from certain experimental results. There are two general methods for doing this, the method of the chemist and the method of the physicist. The chemist's method is a good deal more difficult to understand, and it will be better to postpone its description until later (Chapter 12). The physicist's method not only is more easily understood, but also, in general, yields slightly more accurate results.

Illustration of the principle involved in the physical method. First let us illustrate the principle which underlies the physicist's method. Suppose that we have a gun (Fig. 34) which fires bullets by the release of a stiff spring. Let the bullets be ping-pong balls, and let us shoot them with a certain velocity at a target, which they

strike again and again, at point *A*, in line with the barrel of the gun, as shown in the figure. Now we will suppose a steady wind

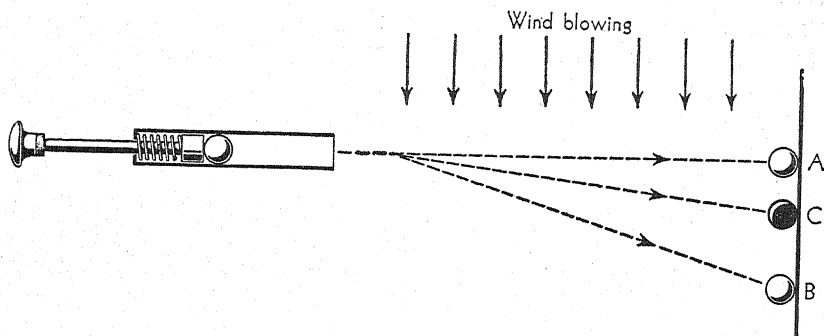


FIG. 34. Diagram Illustrating the Physical Method of Determining Atomic Weights

to blow across the region between the gun and the target, and again shoot the balls. Since the ping-pong balls are very light in weight, they will be blown far off their original course and will strike the target, say, at *B*, and will do so again and again, at the same spot.

Let us now shoot a *heavier* ball, but one of the *same size* as before, so that the force of the wind acting upon it will be just the same as before. We could drill a small hole in a ping-pong ball, fill the inside with water to make the ball heavier, and seal the hole. We will then properly stretch the spring on the plunger to shoot this water-filled ball at the target with the same velocity as that possessed by the original ping-pong balls. This heavier ball, of greater mass and of more *inertia*, will not deviate (*C*) nearly as much as the lighter ball, though the force of the wind blowing on it is the same. Inertia, as previously pointed out in Chapter 2, is a fundamental property of all masses of matter. A heavy body is moved with more difficulty than a lighter body.

The spots where the balls strike the target could be conveniently registered by making the target out of a soft impressionable wax, or of white paper and covering the balls with lampblack. If we know the relative distances of the spots *B* and *C* from the spot *A* (undeviated balls), we can easily calculate the *relative weights* of the two balls *without having to weigh the balls*. The smaller the deviation, the heavier the ball.

Positive-ray method for measuring the relative weights of atoms. In the evacuated glass bulb of Fig. 35, there are two electrode plates

P_1 and P_2 . These are connected to a large battery or other source of electric current of high voltage. P_1 is connected to the positive

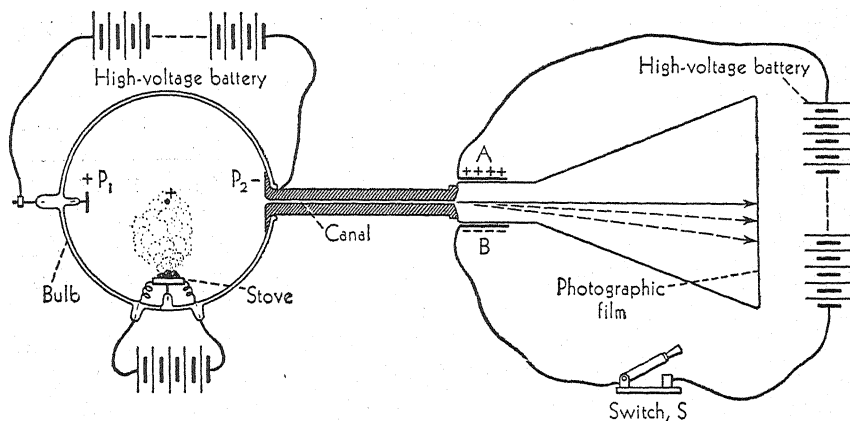


FIG. 35. Diagram Illustrating the Positive-Ray Method of Measuring the Relative Weights of Atoms

pole and P_2 to the negative. Electrons jump out of P_2 , shoot across the vacuum, and strike P_1 .

A very small amount of the element under investigation is introduced into the bulb. It must be present as a gas or a vapor. If it is not very volatile, it may be placed on a little electric stove, as shown, and some of it vaporized. As the atoms get into the path of the electrons (shooting from P_2 to P_1), the atoms are bombarded, and some of their own electrons are knocked off. They are thus converted into positively charged *ions*, and the violence of the electron bombardment is so great that both *metallic and nonmetallic* atoms are converted into positive ions.

The plate P_2 , which is *negatively* charged, has a tiny hole drilled in it, and it is attached to a long tube (of very small bore) known as the *canal*. The positive ions in the bulb are attracted strongly toward the negative plate P_2 (by electrostatic attraction) and move rapidly toward it. By the time they reach it, they are traveling at a very high speed. Some of these ions get through the hole and travel down the canal. Such a stream of ions was at one time called *canal rays*, but today we call them *positive rays*. The positive rays shoot out of the far end of the canal, very much like bullets out of a gun, and travel across another evacuated space and finally strike a photographic film, at a spot exactly in line with the canal tube. The

impact of these high-speed ions on the photographic film affects it very much like light; and when the film is developed, a small spot appears on the negative, just where the ions had been hitting.

Now, as the positive ray emerges from the canal, it passes between two plates *A* and *B*, which can be connected with a high-voltage battery by throwing the switch *S*. Plate *A* then becomes positively charged, and plate *B* becomes negatively charged. Then the positive ions deviate in their path and strike the photographic film off center, since the ions as they pass between the plates have been repelled by *A* and attracted by *B*. (Actually the rays are also allowed to pass between the poles of a strong magnet, but we are here omitting this feature for the sake of simplicity. The complete apparatus will be described in Chapter 13.)

The extent of deviation of the ions will depend, for ions of the same charge and speed, on the *masses* of the ions. A light-weight ion will naturally be pulled and pushed out of its path more than a heavier one, like the ping-pong balls previously mentioned. The ions of the various atoms can be produced in the bulb in separate experiments, and the relative deviations of the spots on the film measured; and from these relative deviations the relative weights of the various atoms can be determined. This method is extremely sensitive and accurate. Generally the relative weights of the atoms can be determined with an error no greater than about 1 in 10,000. (It is really the relative weights of the *ions* rather than of the *atoms* that is obtained, but the weight of the missing electron or electrons is so small compared with that of the whole atom that it can be neglected or allowed for).

NOTE. In the physical sciences, especially in chemistry, the word *determine* (paragraph above) is used in a somewhat unfamiliar sense. *Determine* is not used as a synonym for *decide*, but rather to convey the idea of *arriving at an exact result through experimentation*. In this sense *determine* is practically equivalent to *measure*.

The relative weights of the atoms. In assigning numbers to the weights of the atoms it is natural to take one of them as a standard and calculate the weights of all the others *relative* to this one. Since the atom of hydrogen is the lightest of all, the natural thing to do would be to call its weight exactly 1. Chemists did that for a long time, but today we find it more convenient to call the weight of the oxygen atom arbitrarily, but exactly, 16, and refer the other weights to it. One of the reasons for doing this is that more of the atoms then turn out to have relative weights that are more nearly *whole* numbers. In the table following will be found a list of some of the

elements, the symbols for their atoms, and the relative weights of these atoms, or their *atomic weights* as they are called. The complete list of atomic weights for the ninety or more elements will be found on the inside of the back cover of this book and in the periodic table on page 210.

The Relative Weights, or Atomic Weights, of Some Atoms

NAME	SYMBOL	ATOMIC WEIGHT	NAME	SYMBOL	ATOMIC WEIGHT
Aluminum	Al	26.97	Nickel	Ni	58.69
Bromine	Br	79.916	Nitrogen	N	14.008
Calcium	Ca	40.08	Oxygen	O	16.000
Carbon	C	12.010	Phosphorus	P	30.98
Chlorine	Cl	35.457	Platinum	Pt	195.23
Chromium	Cr	52.01	Potassium	K	39.096
Copper	Cu	63.57	Radium	Ra	226.05
Gold	Au	197.2	Radon	Rn	222.
Helium	He	4.003	Silicon	Si	28.06
Hydrogen	H	1.008	Silver	Ag	107.880
Iron	Fe	55.85	Sodium	Na	22.997
Lead	Pb	207.21	Sulfur	S	32.06
Mercury	Hg	200.61	Tin	Sn	118.70
Neon	Ne	20.183	Zinc	Zn	65.38

Atomic weights of ions. As we have just indicated, the atomic weights measured by the positive-ray method, and listed in the table, are really the relative weights of ions rather than of atoms. But the difference is extremely small. On the basis of a weight of 16 for the oxygen atom, or of 1.008 for the hydrogen atom, an electron weighs only 0.000546, or about $\frac{1}{1845}$ of a hydrogen atom. Whether or not an electron or a few electrons are present or missing makes no appreciable difference. It is not necessary to take into account so small a difference in weight. So chemists customarily take the relative weights of Na and Na⁺ as being the same, namely 22.997; and of Cl and Cl⁻ as being the same, namely 35.457.

MOLECULAR WEIGHTS; PERCENTAGE COMPOSITION

Calculation of molecular weights. Since the weight of a molecule is the sum of the weights of the atoms in the molecule, it is a simple matter to calculate the relative weight, or the *molecular weight* (mol. wt), of a molecule if we know the formula of the molecule, that is, the kind and number of atoms in the molecule. (Methods

for finding the formulas of molecules will be described in a later chapter.) For instance a certain compound known as ethane (gas at ordinary temperatures) is made up of molecules every one of

which has the structural formula $\begin{array}{c} \text{H} \quad \text{H} \\ | \quad | \\ \text{H}-\text{C}-\text{C}-\text{H} \\ | \quad | \\ \text{H} \quad \text{H} \end{array}$ or the molecular

formula C_2H_6 . The molecular weight of this molecule is found by addition of the atomic weights:

$$\begin{array}{rcl} 2 \times 12.01 \text{ (atomic weight of carbon)} & = & 24.02 \\ 6 \times 1.008 \text{ (atomic weight of hydrogen)} & = & 6.048 \\ \text{Molecular weight of ethane molecule} & = & 30.068 \end{array}$$

We must keep clearly in mind that a molecular weight represents the weight of a molecule *relative* to the weight of an oxygen atom, taken as 16.

Other examples:

HCl 1.008 $\underline{35.457}$ Mol. wt = 36.465	H_2O $2 \times 1.008 = 2.016$ $\underline{16.000}$ Mol. wt = 18.016	NH_3 $3 \times 1.008 = 3.024$ $\underline{14.008}$ Mol. wt = 17.032
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Similarly, the molecular weights of electrovalent, or ionic, molecules may be calculated by adding the weights of the ions:

$(\text{Na}^+, \text{Cl}^-)$ 22.997 $\underline{35.457}$ Mol. wt = 58.454	$(\text{Fe}^{++}, \text{S}^{--})$ 55.85 $\underline{32.06}$ Mol. wt = 87.91	$(\text{Ca}^{++}, 2 \text{Cl}^-)$ 40.08 $2 \times 35.457 = \underline{70.914}$ Mol. wt = 110.994
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Thus, the molecular weight of any covalent or electrovalent molecule may be calculated if its molecular formula is known.

Percentage composition. Chemists very often find it convenient to express the composition of a molecule in terms of the percentage (by weight) of the different atoms present in the molecule. For example, a molecule of sodium chloride (Na^+, Cl^-) has a molecular weight of 58.454. Of this weight, 22.997 is contributed by Na^+ and 35.457 by Cl^- . Therefore the percentage of the total molecular weight contributed by Na^+ is $\frac{22.997}{58.454} \times 100$ per cent = 39.3 per cent;

and the percentage due to Cl^- is $\frac{35.457}{58.454} \times 100$ per cent = 60.7 per cent. Or we may calculate the percentage composition by proportion :

$$\begin{array}{rcl} 58.454 : 100 & = & 22.997 : x \\ 58.454 : 100 & = & 35.457 : y \end{array} \qquad \begin{array}{l} x = 39.3 \text{ per cent} \\ y = 60.7 \text{ per cent} \\ \hline 100.0 \text{ per cent} \end{array}$$

The percentage composition of sodium chloride (Na^+ , Cl^-) is 39.3 per cent Na^+ and 60.7 per cent Cl^- ; or, as it may be stated, 39.3 per cent sodium and 60.7 per cent chlorine.

In the same way the percentage composition of an ammonia molecule, NH_3 , may be calculated :

$$\begin{array}{rcl} \frac{3 \times 1.008}{17.032} \times 100 & = & 17.8 \text{ per cent hydrogen} \\ \frac{14.008}{17.032} \times 100 & = & \frac{82.2 \text{ per cent nitrogen}}{100.0 \text{ per cent}} \end{array}$$

For the alcohol molecule, $\text{C}_2\text{H}_6\text{O}$, the percentage composition is obtained thus :

$$\begin{array}{rcl} \frac{1 \times 16.00}{46.068} \times 100 & = & 34.7 \text{ per cent oxygen} \\ \frac{2 \times 12.01}{46.068} \times 100 & = & 52.2 \text{ per cent carbon} \\ \frac{6 \times 1.008}{46.068} \times 100 & = & \frac{13.1 \text{ per cent hydrogen}}{100.0 \text{ per cent}} \end{array}$$

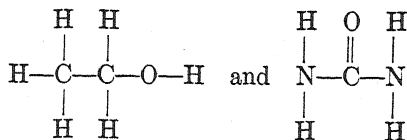
Previously, in Chapter 2, it was stated that iron sulfide contains 63.5 per cent iron and 36.5 per cent sulfur. If we know the formula for a molecule of iron sulfide (Fe^{++} , S^{--}), the calculation may be made thus :

$$\begin{array}{rcl} \frac{55.85}{87.91} \times 100 & = & 63.5 \text{ per cent iron} \\ \frac{32.06}{87.91} \times 100 & = & \frac{36.5 \text{ per cent sulfur}}{100.0 \text{ per cent}} \end{array}$$

In many of the later chapters of this book we shall on frequent occasions be concerned with the percentage compositions of various kinds of molecules.

Questions

1. In your own words, summarize the evidence presented in this chapter for the existence of particles of matter. Can you give any further evidence?
2. Define and illustrate (a) atom; (b) molecule; (c) ion. What is meant by the term (d) *molecule of an element*; (e) *molecule of a covalent compound*; (f) *molecule of an electrovalent compound*?
3. (a) If electrodes, leading from the positive and negative poles of a battery, are dipped into water in which an electrovalent compound is dissolved, the passage of an electric current through the solution is indicated by a suitable instrument in the circuit. Why? (b) In similar circumstances the flow of a current through a solution of a covalent compound is not indicated. Why?
4. Give the derivation of the names of the following elements (consult a dictionary): (a) bromine; (b) helium; (c) xenon; (d) chlorine; (e) hydrogen; (f) phosphorus; (g) europium; (h) tantalum; (i) thorium.
5. The structural formulas of the molecules (covalent) of ethyl alcohol and of urea are respectively



What are the valences of the atoms in these molecules?

6. What are the valences of the ions in the following electrovalent molecules: (a) Ca^{++} , 2Cl^{-} ; (b) Ca^{++} , S^{--} ; (c) Fe^{+++} , 3Cl^{-} ; (d) 2Al^{+++} , 3O^{--} ?
7. What advantage would chemists gain if they could know the absolute weights of the atoms, in addition to their relative weights?

Problems

1. The Swedish chemist Berzelius at one time set up a system of atomic weights in which oxygen was arbitrarily assigned the weight of 100 (instead of the arbitrary value 16). On this basis what would be the relative weights (atomic weights) of the following atoms: Fe, S, H, Si, Cl, Ag?
2. Taking the atomic weights given on page 49 (or in the list on the inside back cover of the book) calculate the molecular weights of the molecules having the following formulas: (a) O_3 (ozone); (b) COCl_2 (phosgene); (c) C_3H_8 (propane); (d) C_6H_6 (benzene); (e) CS_2 (carbon disulfide).
3. Calculate the molecular weights of the molecules with the following formulas: (a) Na^{+} , Cl^{-} , sodium chloride; (b) Mg^{++} , 2Cl^{-} , magnesium chloride; (c) Al^{+++} , 3Cl^{-} , aluminum chloride; (d) Mg^{++} , O^{--} ,

magnesium oxide; (e) (Mn^{++++} , 2O^{--}), manganese dioxide; (f) (K^+ , ClO_3^-), potassium chlorate.

4. Calculate the percentage composition of each of the molecules listed in Problem 2.

5. Calculate the percentage composition of each of the molecules listed in Problem 3.

6. In one drop of water there are about one thousand billion billion molecules ($10^3 \times 10^9 \times 10^9$). To help you to visualize the magnitude of this number, calculate the depth (in meters) to which this many lumps of sugar (centimeter cubes), when packed closely together in a flat layer, would cover an area of $1,000,000\text{ km}^2$ (about 621×621 square miles).

Reading References

BRAGG. *Concerning the Nature of Things*. Chapter I (45 pages) has the title "The Atoms of Which Things Are Made."

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FOSTER. *The Romance of Chemistry*. Chapter III tells of electrons, atoms, and molecules.

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JAFFE. *Crucibles*. Chapter VII tells about Dalton and his conception of atoms.

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Gram-Atomic Weights and Gram-Molecular Weights

Chemists cannot work with single atoms and molecules. Chemists have not yet learned how to handle *individual* atoms and molecules. These particles are entirely too small to be handled one at a time. The smallest visible piece of matter that can be picked up or supported on a fine needle point would contain billions of atoms. A chemist cannot bring a single atom close up to another one so that the two will unite to form a molecule as a brakeman can bring two freight cars together so that they will join through set couplings.

True it is that chemists speak of "making atoms react," of "making molecules react," and of "making compounds," just as though they *could* join two atoms firmly together. But this is picturesque language and is so understood by all chemists. All anyone can do is, to mix vast numbers of atoms of one kind with vast numbers of atoms of another kind, or vast numbers of molecules of one kind with vast numbers of molecules of another kind, and *give them a chance to react* if they are inclined to do so. What these particles do they do of their own accord because of their own inherent properties.

A chemist can do certain things to help or hinder the progress of a chemical reaction. By introducing certain foreign substances (called *catalysts*) into the system, or by varying the temperature or the pressure or the concentration, he can often cause a reaction to go faster or slower, as he pleases; or he can push a reaction toward completion or away from completion. *But in all reactions he is dealing with many billions of atoms at the same time — never single ones.*

Dealing with definite numbers of particles. Since chemists do not have the ability to deal with single atoms and molecules, the next best thing is to deal with *known numbers* of these particles. In Chapter 5 we shall see how the atoms and the molecules can actually be counted. But even at present we have the means of setting apart the *same number* of any kind of atoms or molecules, even though the actual number of particles so taken is not known. There is a very great advantage in being able to do this, and let us see how it can be done.

Gram-atomic weights. Chemists have agreed among themselves upon certain definite weights of elements which they call *gram-atomic weights* (*g-at. wt.*). The *gram-atomic weight* (*g-at. wt.*) of any element is the number of grams of that element corresponding to its atomic weight. From the table of elements (p. 49) it will be seen that the atomic weights of hydrogen, oxygen, sodium, and copper are respectively 1.008, 16.000, 22.997, and 63.57. Therefore by definition the gram-atomic weights of these elements are 1.008 g, 16.000 g, 22.997 g, and 63.57 g.

The reason for selecting gram-atomic weights as convenient quantities of the elements to deal with is that the gram-atomic weights of *all* the elements contain the same number of atoms. For example, when one weighs out 22.997 g of the metal sodium, there are just as many atoms of sodium present as there are atoms of copper in 63.57 g of copper. The number of each is the same. Chemists call this number of atoms present in a gram-atomic weight the *Avogadro number* and symbolize it by the letter *N*. At the present stage of our study we have not stated what the number actually is, nor does it matter, for many purposes, what it is.

Why do gram-atomic weights of different elements contain the same number of atoms? The answer to this question can be made clear by a simple illustration. Suppose we have two large bins, one filled with oranges of very *uniform* size, every orange weighing just 1 lb, and the other with grapefruit, also *uniform* in size, and weighing just 2 lb. One ton of oranges would contain 2000 oranges. How many tons of grapefruit must we take to get 2000 grapefruit? Obviously, the answer is 2 tons. But it is not necessary to know the absolute weights in pounds of the two objects. The *relative weights* are 2 to 1. Therefore we must take twice as many tons of grapefruit as of oranges in order to have the same number of each. The *relative weights* in tons contain the same number.

Similarly with the atoms: Sulfur atoms weigh a little more than twice as much as oxygen atoms, 32.06 and 16. Consequently 32.06 tons of sulfur will contain just as many sulfur atoms as there are oxygen atoms in 16 tons of oxygen; and 32.06 grams of sulfur and 16 grams of oxygen contain the same number of atoms.

Further illustration of the validity of this conclusion. To make our conclusion perfectly clear let us take another homely illustration. Fig. 36 shows four balls, a ping-pong ball (PPB), a golf ball (GB), a tennis ball (TB), and baseball (BB). The *relative weights* of these balls are indicated in terms of the ping-pong ball (which is the lightest), namely PPB = 1, GB = 17, TB = 21, BB = 53.

Suppose we have 1 ton of PPB. (That would be a good many ping-pong balls, actually enough to fill up about 200 barrels.) There

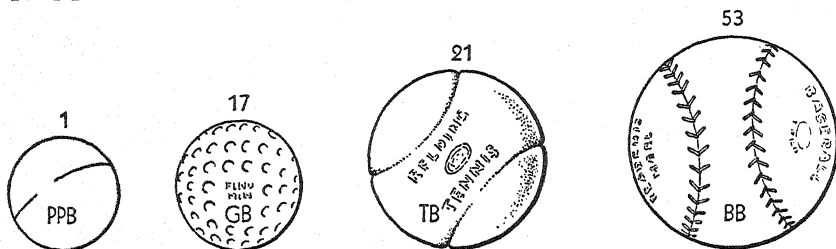


FIG. 36. Drawing Showing Relative Weights of Ping-pong Balls, Golf Balls, Tennis Balls, and Baseballs

is a certain number of PPB in 1 ton. We don't know what the number is. Now suppose we say that we should like to have just as many golf balls (GB) as we have ping-pong balls (PPB). How many tons of GB should we need? If we took only 1 ton of GB, we should not have nearly as many GB as PPB, because every GB weighs 17 times as much as PPB. Obviously, we should have to take 17 tons of golf balls to have the same number as are present in 1 ton of ping-pong balls; and similarly we should need 21 tons of tennis balls or 53 tons of baseballs to equal this number. In other words, if we take the *relative weights of these various balls in tons*, we get the same number in every case.

There can be no question about the validity of this conclusion. But we may, if we wish, check ourselves by dividing the absolute weights as found by actual weighing (PPB = 0.0953 oz, GB = 1.6201 oz, TB = 2.0013 oz, BB = 5.509 oz) into 1 ton, 17 tons, 21 tons, and 53 tons, respectively, to find the actual number of balls present in each case. (There are 32,000 oz in a ton of 2000 lb.) The answers are 335,782 ping-pong balls, 335,782 golf balls, 335,782 tennis balls, 335,782 baseballs.

So, in the case of the atoms, which are really little balls themselves, chemists can be absolutely sure that there is the same number of atoms in every gram-atomic weight because the gram-atomic weights of the different elements are merely the *relative weights of the atoms in grams*. As we said before, we do not know, at the moment, what this number is. It is naturally an enormously large number because the atoms are all so small. We have agreed to call this number *N* (the Avogadro number).

Gram-molecular weight. Just as with atoms, so with molecules, we find it a very great advantage indeed to deal with *gram-molecular*

weights (g-mol. wt). The gram-molecular weight of any compound is the number of grams of that compound corresponding to its molecular weight. Thus, the gram-molecular weights of the compounds water, ammonia, and sodium chloride are, respectively, 18.016 g, 17.032 g, and 58.454 g (p. 50). These gram-molecular weights, all of them, contain the same number of molecules, namely N . This is true of all gram-molecular weights of all compounds. They necessarily contain as many molecules, N , as gram-atomic weights contain atoms, N . For example, the relative weight of a water molecule, referred to $O = 16$, is 18.016. If we take 16 g of oxygen atoms, we have a number of atoms equal to N ; and if we take the relative weight of H_2O in grams, namely 18.016 g, we also have N water molecules.

Percentage composition on a gram basis. We have already calculated the percentage compositions of several *single* molecules. For example, for a molecule of methane, CH_4 , the calculation would be

$$\frac{12.01}{16.042} \times 100 = 74.9 \text{ per cent carbon}$$

$$\frac{4 \times 1.008}{16.042} \times 100 = 25.1 \text{ per cent hydrogen}$$

It makes no difference how many molecules, all of the same kind, that we select for the basis of calculating the percentage composition. The result is the same for one as for ten or as for a billion. Often it is very convenient to use gram-atomic weights and gram-molecular weights for the calculation — that is, to do it on a *gram* basis. Thus, for methane:

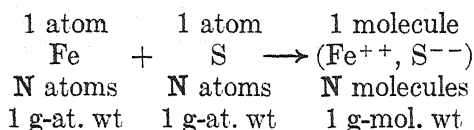
$$\frac{12.01 \text{ g}}{16.042 \text{ g}} \times 100 = 74.9 \text{ per cent carbon}$$

$$\frac{4 \times 1.008 \text{ g}}{16.042 \text{ g}} \times 100 = 25.1 \text{ per cent hydrogen}$$

If we should here employ ounces or pounds or tons, or take any quantity of the compound whatsoever, the percentage composition would still be the same.

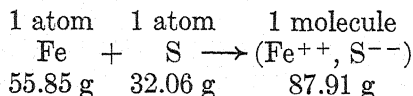
Double meaning of symbols. The student may recall that we said, in the last chapter, that the symbols for the atoms are reserved to refer to the single atoms; but we made the parenthetical remark that they also are sometimes allowed to represent a certain number of atoms. This number is N . The same is true of molecular formulas. A formula not only symbolizes a *single* molecule, but also N molecules. In other words, the chemist by a rapid shift of gears in his

brain, so to speak, thinks of a single atom and a gram-atomic weight, or of a single molecule and a gram-molecular weight, at the same time. For example, in the following equation the symbols represent single particles and also N particles, as shown :



It is very helpful to assign this double meaning to our symbols for atoms, ions, and molecules ; and it is also reasonable to do so because whatever the single particle will do, N particles will also do, but on a much larger scale.

Significance of N . When we weigh out, on our balance, gram-atomic weights and gram-molecular weights, we know that we are dealing with a certain number, N , of particles. This is truly a magnificent result ; for it means that we can weigh out quantities of different elements or of different compounds that will contain the same numbers of particles. If we wish to mix atoms or molecules together and be sure that they are mixed in equal numbers, we have the means for doing so. For instance, suppose that we should like to bring iron atoms and sulfur atoms together in just the right proportion, one atom of Fe for every atom of S, to form iron sulfide ($\text{Fe}^{++}, \text{S}^{--}$) :



All we have to do is to weigh out a gram-atomic weight of iron (55.85 g) and a gram-atomic weight of sulfur (32.06 g) ; in both cases we have weighed out the same number of atoms, namely N . Also, in this reaction, 1 g-mol. wt of the product of the reaction, iron sulfide ($\text{Fe}^{++}, \text{S}^{--}$), is formed ; and it too consists of N molecules (87.91 g).

Pilot ratio. In order to achieve equality in numbers of iron atoms and sulfur atoms it is not necessary that we take gram-atomic weights. It is only necessary that the weights of iron and sulfur be *in the same ratio* as the gram-atomic weights, 55.85 : 32.06 (which may be called the *pilot ratio*). For instance, we could weigh out (1) one tenth or (2) one hundredth of these quantities, namely (1) 5.585 g of iron and 3.206 g of sulfur or (2) 0.5585 g of iron and 0.3206 g of sulfur. These would be in the same ratio as the pilot ratio 55.85 : 32.06.

$$\begin{aligned}(1) \quad \frac{55.85 \text{ g (N)}}{32.06 \text{ g (N)}} \text{ (pilot ratio)} &= \frac{5.585 \text{ g (0.1 N)}}{3.206 \text{ g (0.1 N)}} \\(2) \quad \frac{55.85 \text{ g (N)}}{32.06 \text{ g (N)}} \text{ (pilot ratio)} &= \frac{0.5585 \text{ g (0.01 N)}}{0.3206 \text{ g (0.01 N)}}\end{aligned}$$

In (1) we should be working with 0.1 N atoms of iron and 0.1 N atoms of sulfur, and in (2) with 0.01 N atoms of iron and 0.01 N atoms of sulfur. In both cases we should achieve equality in numbers of the iron and sulfur atoms to be mixed together for reaction.

Further illustrations. Suppose that we wish to allow 10 g of iron to react with sulfur, and that we want to know exactly what quantity of sulfur will be required. The statement of the proportion will be

$$\begin{aligned}\frac{32.06}{55.85} \text{ (pilot ratio)} &= \frac{x}{10} \\55.85 \times x &= 32.06 \times 10 \\x &= 5.74 \text{ g of sulfur}\end{aligned}$$

A pilot ratio, or known ratio, is set up in the proportion to guide us, as we have already indicated, to a solution for the unknown term (x) in the other ratio.

Or suppose we have a purpose in mind for which we need 2000 g of iron sulfide (Fe^{++} , S^{--}), and wish to know how much iron and sulfur will be required to make it. We may first calculate the quantity of iron required:

$$\begin{aligned}\frac{87.91 \text{ g iron sulfide}}{2000 \text{ g iron sulfide}} \text{ (pilot ratio)} &= \frac{55.85 \text{ g iron}}{x \text{ g iron}} \\x &= 1270.6 \text{ g iron}\end{aligned}$$

Then, with a similar proportion, we may calculate the quantity of sulfur; or we may simply subtract the iron from the iron sulfide, $2000 - 1270.5 = 729.5$ g of sulfur, since, of course, the combined weights of the iron and sulfur are equal to the weight of the iron sulfide produced (law of conservation of mass).

The definiteness of chemical processes. From all that has been stated in this chapter, it will be seen that chemical processes involve *definite weights* of matter. We may state the composition of a chemical compound, say methane, CH_4 , in exact percentages because experiment has shown that these always express the composition of a compound, irrespective of the source from which it is obtained or the method by which it is prepared. This characteristic is embodied in the *law of definite composition*: *the composition of a pure chemical compound is always precisely the same.*

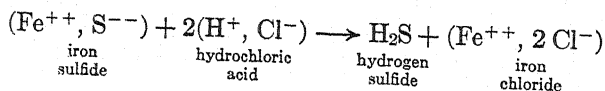
In like manner the chemical reactions which compounds undergo are always perfectly definite under stated conditions. Thus, in the problem of the preceding section, we found that 10 g of iron combine with 5.74 g of sulfur to form 15.74 g of iron sulfide. If less than 5.74 g of sulfur is present, then a corresponding amount of iron will remain unchanged. On the other hand, if more than 5.74 g of sulfur is present, then all the iron will be changed into sulfide, and the excess of sulfur will remain unaltered.

Questions

1. Explain clearly why all gram-atomic weights and gram-molecular weights contain the same number of atoms and molecules respectively.
2. Just what is the advantage of being able to measure out atoms and molecules in equal numbers, or in any relative numbers which we please?
3. Which element has the smallest gram-atomic weight? Which one has the largest? What are the gram-atomic weights of iron, lead, mercury, copper, silver, gold? Make a list of the elements having atomic weights up to 40 (calcium) and memorize their atomic weights.

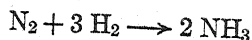
Problems

1. The formulas for some compounds are C_2H_2 ; CO_2 ; PH_3 ; $\text{C}_2\text{H}_6\text{O}$; and for some other compounds are $(\text{K}^+, \text{Cl}^-)$; $(\text{Ca}^{++}, 2\text{Br}^-)$; $(2\text{Na}^+, \text{SO}_4^{--})$; $(2\text{Al}^{+++}, 3\text{O}^{--})$. Calculate their gram-molecular weights from the gram-atomic weights of the elements which they contain.
2. Using gram-atomic and gram-molecular weights, calculate the percentage composition of the compounds given in Problem 1.
3. If iron sulfide and hydrochloric acid react completely as indicated in the following equation:



what weight of hydrogen sulfide can be produced from 25 g of iron sulfide?

4. If one wishes to prepare 10 lb of hydrogen sulfide (H_2S), what weight (in pounds and also in grams) of iron sulfide will be required?
5. If nitrogen and hydrogen react completely to form ammonia according to the following equation:



what weights of nitrogen and hydrogen are needed to produce 500 g of ammonia?

CHAPTER 5

Gases; the Gas Laws; the Kinetic-Molecular Theory; Determination of Molecular Weights

The three states of matter. It is common knowledge that water may exist in three very different physical states, namely, gaseous, liquid, and solid. Existence in all these three states is not peculiar to water but is the common behavior of the great majority of substances. Experiment has shown that every substance, whether element or compound, tends to pass into the gaseous state if its temperature is raised sufficiently, although it is not always possible actually to bring about such a change. In some cases the temperature required is so high that it cannot be attained by laboratory methods; in others, the substance decomposes before the required temperature is reached. Experiments also show that under the combined effect of cold and pressure every gas may be condensed into a liquid; and this may then be frozen into a solid.

In a general way a *gas* or a *vapor* may be regarded as matter in such a state that it distributes itself uniformly throughout the space or volume in which it is confined. A *liquid* does not so distribute itself; it has a volume of its own but no characteristic shape, and in so far as it fills a vessel it takes the latter's shape. A *solid* retains its own shape (and volume), irrespective of the size or form of the containing vessel.

If a given substance exists completely in the gaseous state at *ordinary temperatures and pressures*, we call it a gas; if it is ordinarily a liquid or a solid, but evaporates readily, we refer to the evaporated portion as a *vapor*. Thus, we speak of oxygen *gas*, water *vapor*, and camphor *vapor*.

The barometer. In the study of gases we obviously must often deal with temperature and pressure. Already we have described a thermometer (p. 18). A barometer, or "pressure-meter," may be simply constructed by filling a glass tube about 80 cm long (and closed at one end) with mercury, and then inverting it and thrusting the open end into a well of mercury, as shown in Fig. 37. The mercury column, which falls away to give a vacuum at the top, is supported by the weight, or downward-

pushing force, of a column of air (of cross section equal to that of the mercury column) extending to the top of the atmosphere. This downward

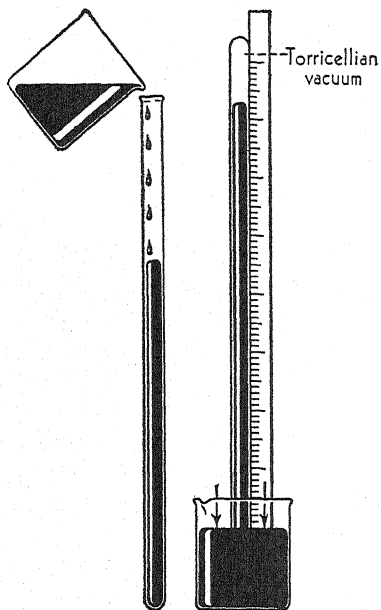


FIG. 37. A Simple Type of Barometer Made by Filling a Glass Tube with Mercury and Inverting It in a Well of Mercury

pressure of the atmosphere is exerted on the surface of the mercury in the well. As the atmospheric pressure changes up or down, the mercury column moves up or down. The atmospheric pressure, in terms of centimeters or millimeters of mercury height, may be read off on a meter stick placed alongside.

The vacuum above the mercury is called a Torricellian vacuum in honor of the Italian Torricelli, who, while a young student assistant of Galileo, made the first barometer in very much this way. Incidentally, it is interesting to know that Torricelli's vacuum was the first authentic case of the produc-

tion of a vacuum. Up to that time, about 1643, it had been supposed that "Nature abhors a vacuum."

Fig. 38 shows the so-called Fortin-type barometer, used today in taking accurate barometric readings. In principle it is exactly the same as the simpler type just described, but it carries more elaborate fittings for adjusting the mercury in the well to constant level and for reading the exact position of the top of the mercury column.

Characteristics of the gaseous state. It is very significant that the physical conduct of *all* gases is very largely the same and bears no relationship to the chemical composition of the gases. Consequently the characteristics listed below apply generally to the gaseous state.

1. **Compressibility.** The differing behavior, toward compression, of liquids and solids, on the one hand, and gases, on the other, re-

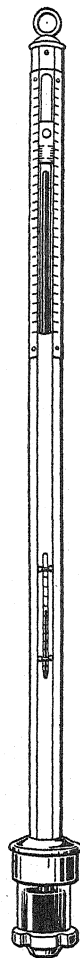


FIG. 38. A More Elaborate Type of Barometer

veals one of the important ways in which gases differ from the other states of matter. Liquids and solids offer great resistance to any force tending to squeeze them into smaller volume; they are but slightly compressible. On the other hand, the volume of a gas is greatly altered by comparatively small changes in pressure. A familiar illustration of this is found in the common experience of pumping air into a bicycle or automobile tire. A surprisingly large volume of air may be pumped into what is an almost unchanged volume in the tire.

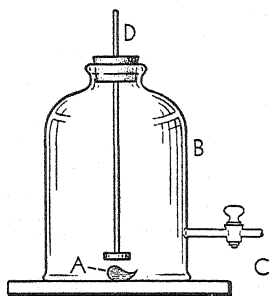


FIG. 39. Apparatus Used for Showing the Rapid Expansion of a Vapor in a Vacuum

2. Expansibility. The ability of a gas to expand is no less characteristic than its compressibility. In fact, a gas tends to expand indefinitely, and to distribute itself uniformly throughout all the space in which it is confined. If the gas or vapor is suddenly set free in a vacuum, this distribution occurs with

great rapidity, as demonstrated by the following experiment: A small thin-walled bulb A (Fig. 39) is filled with bromine, sealed, and placed in a glass vessel B, which can be closed and exhausted by a water pump attached at C. A glass rod is arranged to slip through a tight-fitting rubber stopper D. When the vessel has been exhausted, the rod is pushed down so as to crush the bulb. Instantly the reddish vapor of bromine fills the vessel.

3. Diffusion. If two gases, A and B (Fig. 40), are brought in contact, each will penetrate into the other until an even mixture in both vessels is reached. This process is called *diffusion*, and it resembles expansion into a vacuum. It takes place *slowly*, for each gas presents an obstacle to the expansion of the other. The rates of diffusion are not dependent on gravity, for a heavy gas in A will diffuse upward into a lighter one in B. Two gases of unequal density when once mixed show little tendency to separate into layers. Previously, in Chapter 3, we have noted the diffusion of camphor vapor into air.

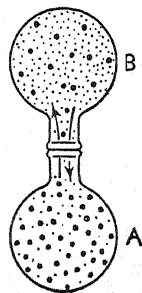


FIG. 40. The Diffusion of Gases

THE GAS LAWS

Importance of the gas laws. Because so many of the fundamental principles of chemistry are intimately related to the behavior of

gases, it is essential for the student of chemistry to become familiar with some of the laws relating to gases. At present it will be sufficient to consider five such laws which serve to describe the conduct of gases under the usual variety of conditions.

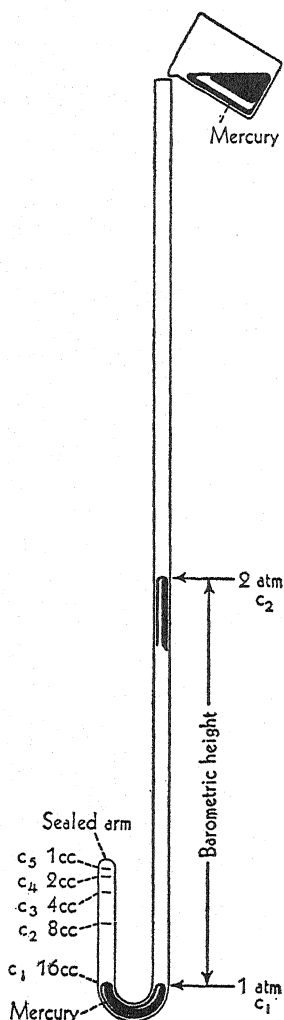


FIG. 41. Diagram of Apparatus Used for Showing How the Volume of a Gas Varies with the Pressure to Which It Is Subjected

1. Variation of volume with pressure; the law of Boyle. Recognizing that gases are compressible, suppose we set ourselves the task of measuring quantitatively how the volume of a gas varies with pressure. We might use an apparatus like that shown in Fig. 41. In the shorter and sealed arm of a J tube, a sample of gas is confined over liquid mercury. Adjusting the mercury level so that it is the same in both arms of the tube (the gas will now be at atmospheric pressure), we read the volume of the confined gas and find it to be 16 cc. Now let us add mercury to the open arm until the level in this arm is higher than the level in the short arm by an amount equal to the barometric pressure (unless we are near sea level this will be somewhat less than 760 mm). The gas is now confined at 2 atmospheres (atm) pressure, and its volume is found by actual observation to be 8 cc. (It is understood that we are keeping the temperature of the gas constant, in this case at room temperature.) Similarly at other pressures the gas will be found to occupy the volumes given in the following table:

EXPERIMENT NO.	PRESSURE	VOLUME
c_1	1 atm P_1	16 cc V_1
c_2	2 atm P_2	8 cc V_2
c_3	4 atm P_3	4 cc V_3
c_4	8 atm P_4	2 cc V_4
c_5	16 atm P_5	1 cc V_5

Thus we find, from such a notebook record of our experimental measurements, that each time the pressure is doubled, the volume is diminished by half. In other words, the product of the pressure and the volume

is constant throughout the series of measurements. Stated in algebraic form, we have the equation

$$P_1 V_1 = P_2 V_2 = P_3 V_3 = K \quad (1)$$

in which P_1 and V_1 are the pressure and volume of a given mass of gas under one set of conditions, P_2 and V_2 those under another. K is their constant product. The numerical value of K will, of course, depend upon the weight of gas taken for experimentation and the units of measurement employed.

Finally we may picture the results of our experiment graphically, Fig. 42. Representing the pressure along the *abscissa* (horizontal line) and the volume along the *ordinate* (vertical line), we plot the points c_1, c_2, c_3, c_4, c_5 from our data and thus obtain the curve AB . The areas of the rectangles corresponding to $P_1 V_1, P_2 V_2, P_3 V_3$ are all equal, and therefore *constant*. The curve is known in geometry as a rectangular hyperbola.

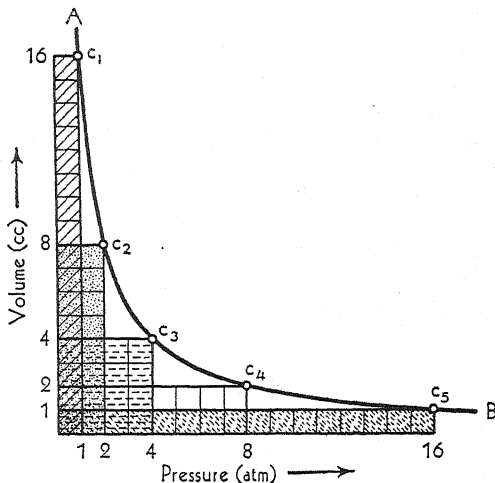


FIG 42. Graphic Representation of the Experiment Illustrated in Fig. 41

The generalization illustrated above is known as *Boyle's law* because it was first formulated in 1660 by Robert Boyle (Fig. 45), who made some careful measurements on the compressibility of air. Boyle's law may be stated thus: *The volume which a given mass of a gaseous substance occupies is inversely proportional to the pressure under which it is measured, provided the temperature remains constant.* To understand better the significance of the expression "inversely proportional" rearrange equation $P_1 V_1 = P_2 V_2$ to

$$\frac{P_1}{P_2} = \frac{V_2}{V_1} \quad (2)$$

Now it is seen that the ratios of pressures and volumes have their subscripts arranged inversely. We may also write $P_1 V_1 = K$, or $V_1 = K \times \frac{1}{P_1}$, which shows that the volume is inversely proportional to the pressure.

Standard pressure. Since the volume of a gas depends upon the pressure at which it is measured, any statement of the properties of a gas, such as density, requires that the corresponding pressure be given. For practical purposes it is more convenient to choose some standard pressure to which all gas volumes are to be referred. This is most conveniently chosen as the average pressure of the atmosphere at sea level as indicated by the barometric reading. This is equal to the pressure exerted by a column of mercury 76 cm (760 mm) in height, which, since the density of mercury is 13.6, is equivalent to a weight, or force, of 1033 g (76×13.6) per square centimeter (cm^2) — that is, to a pressure of 1033 g/ cm^2 . It is the usual practice to express pressures in terms of barometric readings.

Example. Suppose that a gas, measured under a pressure indicated by a barometric reading of 720 mm, has a volume of 620 cc. What volume will this gas occupy under standard pressure (760 mm), with the temperature constant?

According to Boyle's law, $P_1 V_1 = P_2 V_2$. Substituting the values given in the problem, we have $720 \times 620 \text{ cc} = 760 \times V_2$, or $V_2 = 587.4 \text{ cc}$.

NOTE. Because an increase in pressure results in a contraction in volume, it is easy to see that the answer above is *qualitatively* correct because 587.4 cc is less than 620 cc.

2. Variation of volume with temperature; the law of Charles. Experiments show that all gases expand when the temperature is raised (if the pressure is kept constant) and that equal volumes of all gases expand to the same extent for a given increase in temperature. Let us suppose that the volume of the gas has been measured at zero on the centigrade scale. Experiment shows that a rise of one degree causes an expansion equal to $\frac{1}{273}$ of this volume; a rise of two degrees, an expansion of $\frac{2}{273}$. That is to say, if 273 cc of the gas is measured at zero, the volume at 1° above will be 274 cc; at 2° above, 275 cc. At 1° below, it will contract to 272 cc, and at 2° below, to 271 cc (see Fig. 43). If the same rate of contraction should hold good at all temperatures, then at -272° the volume would be 1 cc, and at -273° the volume would be zero. Obviously this conclusion cannot hold, since before such temperatures are reached all gases will have become liquids, in which state the law will not apply. For example, helium, the most difficult of all gases to liquefy, becomes a liquid at -268.9° .

The absolute scale. For many purposes it is desirable to use what is called the *absolute, or Kelvin, scale* of temperature rather than the Fahrenheit or the centigrade scale. On this scale the de-

degrees are the same size as on the centigrade scale, but the zero point is at -273° centigrade, so that water freezes at 273° A (absolute)

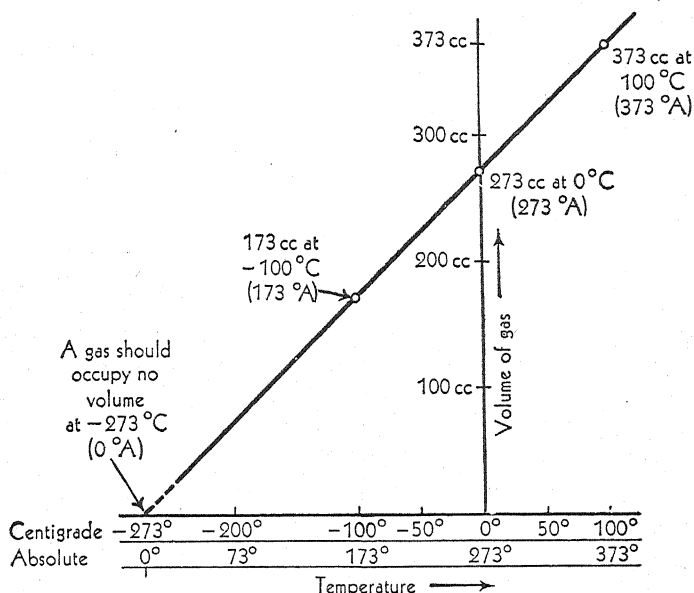


FIG. 43. Graphic Representation of the Variation of the Volume of a Gas with Temperature

and at 0° C (centigrade). At 272° on this scale the 273 cc of gas discussed in the last paragraph would measure 272 cc; at 271° , 271 cc. On such a scale the volume of the gas is proportional to the temperature at every point. It will be noticed that the absolute temperature is obtained by adding 273° to the centigrade temperature. Fig. 44 compares the centigrade and absolute scales.

The following general statement can now be made in regard to the variation of volume of a gas with temperature (Charles's law): *The volumes occupied by a given mass of a gas at different temperatures are proportional to the absolute temperatures of the gas (if pressure is constant).* This generalization was formulated independently in 1801 by the Frenchmen Gay-Lussac (Fig. 46) and Charles; but in order not to confuse it with another law, established by Gay-Lussac (see paragraph 3 below), we shall follow the usual custom and call it Charles's law. If V_1 and V_2 are the volumes at the absolute temperatures T_1 and T_2 , then

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \quad (3)$$

Example. The volume of a certain gas, when measured at a temperature of 70°C , is 650 cc. What is its volume at 10° ?

First reduce the centigrade readings to absolute.

$$70^{\circ}\text{C} = 70 + 273 = 343^{\circ}\text{A}; \quad 10^{\circ}\text{C} = 10 + 273 = 283^{\circ}\text{A}$$

Now, substituting the appropriate values in the equation above, we have

$$\frac{650\text{ cc}}{343} = \frac{V_2}{283}, \quad \text{or} \quad V_2 = 536.3\text{ cc}$$

NOTE. Because a decrease in temperature results in a contraction in volume, we see that the answer above is *qualitatively* correct.

3. The variation of pressure with temperature: The law of Gay-Lussac. We have seen that when the *pressure* remains constant, the

volume increases in proportion to the absolute temperature. From this, together with Boyle's law, the law of Gay-Lussac follows: *If the volume of a gas is kept constant, the pressure will increase in proportion to the absolute temperature.*

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} \quad (4)$$

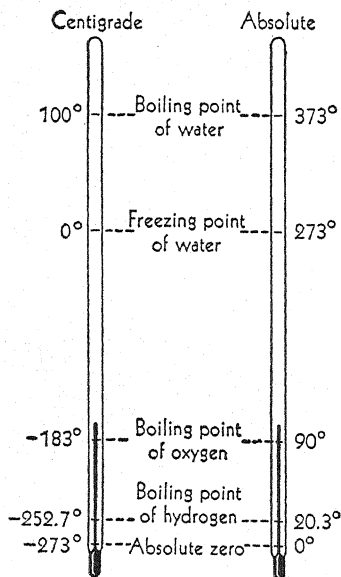


FIG. 44. Comparison of the Centigrade and Absolute Scales

Gay-Lussac made some experiments upon this point and found that the pressure does so increase. This principle is not of as frequent application in chemical calculations as the more familiar law of Charles, but in many fields it is of importance. For example, it enables us to calculate the pressure in a steam boiler at a temperature T_1 if we know the value at some other temperature T_2 . By measurement of the pressure reached in

an explosion we may also calculate the temperature, or vice versa.

Gas cylinders are now generally equipped with safety disks made of a low-melting alloy, so that in case of fire the heat will melt the disk and the greatly increased pressure of the gas inside will force an exit rather than blow up the cylinder.

Variations in volume due to changes in both pressure and temperature. In case both pressure and temperature change, then the



FIG. 45. Robert Boyle (1627-1691)

Distinguished British scientist, founder of scientific chemistry. The first to define an element clearly and to show that a compound is made up of two or more constituents. Chiefly remembered for his experimental work on gases, which led to his formulation of Boyle's law. He helped to perfect the air pump and proved that sound cannot pass through a vacuum. He is the author of an important book entitled *The Sceptical Chemist*, published in 1661



FIG. 46. Joseph Louis Gay-Lussac (1778-1850)

Distinguished French scientist. He showed the variation of the volume of a gas with its temperature, as did also Charles and Dalton about the same time; determined accurately the ratio by volume in which oxygen combines with hydrogen, as well as the combining ratio of many other pairs of gases, and so formulated the law which bears his name. He discovered cyanogen and made many improvements in analytical processes. He was one of the great teachers of his generation and held a number of public offices, including membership in the House of Peers

correction may be made for each in succession. It is more convenient, however, to combine equations (1) and (3), which express, respectively, Boyle's law and Charles's law, and use this new equation for the solution of such problems. This new equation is

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \quad (5)$$

and may be derived as follows: Let us start with a given gas of initial pressure, volume, and temperature P_1 , V_1 , T_1 , and take the gas, in two operations, to the final pressure, volume, and temperature P_2 , V_2 , T_2 . First, we shall keep the temperature constant, and let P_1 change to P_2 . Then $P_1 V_1 = P_2 V_x$, where V_x is some intermedi-

ate volume. Then, keeping the final pressure P_2 constant, we shall allow T_1 to change to T_2 . Therefore $\frac{V_x}{T_1} = \frac{V_2}{T_2}$. Solving this for V_x we get $V_x = \frac{V_2 T_1}{T_2}$; and substituting for V_x in the first equation, we have $P_1 V_1 = P_2 \times \frac{V_2 T_1}{T_2}$, or $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$. This equation really embodies all three laws, those of Boyle, Charles, and Gay-Lussac.

Example. A gas measured 1000 cc at a temperature of 50° C and under a pressure of 740 mm. What volume will it occupy at a temperature of 27° and under a pressure of 760 mm? By substituting the proper values in equation (5) we have

$$\frac{740 \times 1000 \text{ cc}}{273 + 50} = \frac{760 \times V_2}{273 + 27}, \quad \text{or} \quad V_2 = 904.3 \text{ cc}$$

To check: Rewrite equation (5) to give $V_2 = V_1 \frac{P_1}{P_2} \frac{T_2}{T_1}$, which states that the final volume is equal to the original volume multiplied by two fractions, one to correct for a change in pressure and the other to correct for a change in temperature. Since the pressure change is from 740 mm to 760 mm, the volume is decreased and the fraction for pressure is $\frac{740}{760}$. Similarly, the temperature change is from 323° A (50° C) to 300° A (27° C) (giving a decrease in volume), and the fraction for temperature is $\frac{300}{323}$. Thus $V_2 = 1000 \text{ cc} \times \frac{740}{760} \times \frac{300}{323}$, or 904.3 cc.

Standard conditions. In addition to the standard pressure we must have a standard temperature. This is chosen as 0° C, or 273° A, at which temperature ice melts. These two conditions of temperature and pressure are known as the *standard conditions*. When the volume of a gas is given, say 100 l of oxygen, it is understood that the gas occupies this volume under standard conditions (unless specified otherwise), namely, at a temperature of 0° C and under a pressure of 760 mm. The statement that 1 l of oxygen weighs 1.4290 g means that 1 l of this gas measured under standard conditions weighs 1.4290 g.

Equation for standard conditions. Now suppose we designate the volume occupied by a definite weight of gas when measured under standard conditions by V_s ; then V_s , 760, and 273 will be the values of volume, pressure, and temperature corresponding to one set of values in equation (5). Substituting them in place of V_1 , P_1 , T_1 , and dropping the subscripts of the values V_2 , P_2 , T_2 as no longer necessary, we get the equation

$$\frac{760 \times V_s}{273} = \frac{PV}{T}, \quad \text{or} \quad V_s = V \frac{P \times 273}{760 \times T} \quad (6)$$

Example. Suppose we have prepared oxygen in the laboratory and find that the gas measures 685 cc under the laboratory conditions, namely, a temperature of 22° and a barometric pressure of 750 mm, and we wish to know what volume this gas would occupy under standard conditions. By substituting the proper values in equation (6) we get

$$V_s = \frac{685 \text{ cc} \times 750 \times 273}{760 \times (273 + 22)} = 625.57 \text{ cc}$$

This may be *checked* by the method outlined previously.

4. Partial pressure of gases; the law of Dalton. As a result of a large number of experiments which he conducted with *mixtures of gases*, Dalton (Fig. 127) concluded that *the total pressure exerted by a mixture of gases is the same as the sum of the individual pressures exerted by the constituent gases taken separately*. The essential meaning of this statement may be conveyed in another way: *In a mixture of gases every gas exerts the same pressure that it would if it alone were confined in the same volume*. In symbols we may state Dalton's law as follows:

$$P = P_1 + P_2 + P_3 + \dots$$

For example, in the case of air the total pressure of any sample of air is the sum of the pressures of the oxygen gas, the nitrogen gas, the argon, the carbon dioxide, and the water vapor, which, taken together, make up the mixture known to us as air.

Pressure exerted by water vapor; aqueous tension. A gas such as oxygen collected over water (A, Fig. 47) always contains a certain amount of *water vapor*. Water vapor is a true gas and as such contributes its expected share to the total pressure of the mixture. This pressure of water vapor is sometimes called the *aqueous tension*; it is dependent on temperature, which must be specified. To get the pressure exerted by the oxygen alone at the observed volume and temperature we should, in accordance with the law of Dalton, subtract the pressure exerted by the water vapor from the total pressure (which in this case is the same as atmospheric pressure). We shall then have the pressure exerted by *dry* oxygen at the observed volume. If we designate the value of the aqueous tension at the observed temperature by p , and the barometric pressure by P , equation (6) becomes

$$V_s = \frac{V \times (P - p) \times 273}{760 \times T} \quad (7)$$

The value of p increases rapidly with increasing temperature until it reaches 760 mm at the boiling point. A table in the Appendix gives the values at ordinary working temperatures.

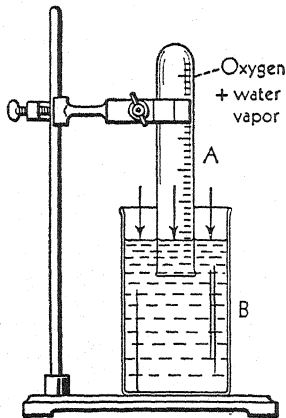


FIG. 47. *Measuring the Volume of a Gas Collected over a Liquid*

Measuring the volume of a gas. Suppose a sample of oxygen has been collected over water in the graduated tube *A* (Fig. 47), and it is required to find the volume the *dry* oxygen would occupy under standard conditions. First raise (or lower) the tube *A* until the level of the water within and without the tube is the same, as shown in the figure. The gas within the tube (oxygen and water vapor) is now at the pressure indicated by the barometer; for the pressure of the atmosphere on the water in *B* is just balanced by the pressure of the gases (within the tube) on the surface of the water, since the levels are the same. It follows that the pressure of the oxygen alone is equal to the barometric pressure less the pressure of the water vapor.

Example. A gas, collected over water at 22° , had a volume of 1250 cc at a barometric pressure of 750 mm. Find the volume of the *dry* gas under standard conditions. The value of the pressure of water vapor at 22° is 19.83 (see the Appendix).

$$\therefore V_s = \frac{1250 \text{ cc} \times (750 - 19.83) \times 273}{760 \times (273 + 22)} = 1111.38 \text{ cc}$$

5. The rate of diffusion; the law of Graham. In 1833 the Scotch chemist Thomas Graham made a series of studies upon what he called the rate of *diffusion* of gases, by which he meant the rate at which various gases will travel through another gas, through a minute pinhole, or through some porous materials such as unglazed pottery. As a result of his experiments he found that under definite conditions of temperature and pressure *the rate of diffusion is inversely proportional to the square root of the density of the gas*. Of two gases the lighter will diffuse the more rapidly. Oxygen and hydrogen have densities which are almost exactly in the ratio 16:1 (really 32:2.016), and their rates of diffusion are approximately in the ratio

$$\frac{1}{\sqrt{16}} : \frac{1}{\sqrt{1}} = \frac{1}{4} : \frac{1}{1} = 1 : 4$$

In other words, hydrogen will leak through fine pores four times as fast as oxygen; and it will also spread into a vacuum and diffuse into another gas about four times as fast as oxygen.

Demonstration of diffusion. This property may be demonstrated by the use of the apparatus represented in Fig. 48. A small battery jar *A* is connected by a tight-fitting rubber stopper or plaster-of-Paris joint with a glass tube *B*, the other end of which passes just through a stopper in the vessel *C*. The vessel is half filled with water and is provided with a second tube *D*, drawn to a small jet at *E* and extending to the bottom of the vessel *C*. A bell jar or large beaker *F* is completely filled with hydrogen and quickly lowered over the porous jar *A* as shown. The hydrogen, being much less dense than the air, diffuses into the porous jar faster than the air within the jar diffuses out, and develops a pressure within the jar. This increased pressure is communicated to the surface of the water in the bottle *C*, forcing some of the water out through the jet *E* and forming a fountain, as indicated.

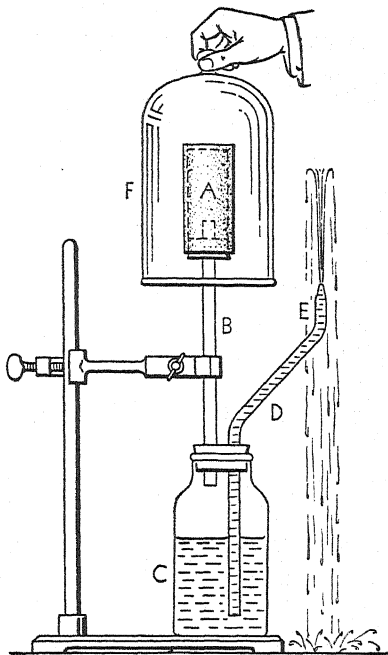


FIG. 48. *Demonstration of Diffusion*

THE KINETIC-MOLECULAR THEORY OF GASES

The meaning of laws in science. The five laws just considered are merely general statements in regard to the conduct of gases *as determined by experiment*. Like all other scientific laws, they offer no explanation of the facts which they state, nor do they place any restriction upon nature which compels obedience, as the laws of a country bind society. They are simply concise statements of what might be called the *habits of nature* as observed in experiment.

Forming a theory. Now that we have found it possible to describe in concise form (laws) the conduct of gases under varying conditions of temperature and pressure, many questions arise in our minds. Why do all gases expand and contract in the same way, regardless

of their other widely differing properties? Why does heating a gas cause it to expand? How does a gas exert pressure?

To answer these questions we begin by a process of *imagining*. We imagine that the similar conduct of all gases is probably due to some simple mechanical structure which they all share, and we try to form a mental picture of this structure. *The process of constructing a mental picture of this kind is called forming a theory.* After constructing a picture which answers all our questions, we then try to make the theory serve as the basis for the prediction of new effects, and try to find new facts and laws which will subject the theory to severe and critical test. Theories come and go: some once highly respected have been discarded because they could not stand the light of increased knowledge; a few have been recalled to life when later investigations demonstrated their validity. One of the most penetrating and far-reaching of all our theories, and one of the most fertile in prediction and forecast, is the famous *kinetic-molecular theory of gases*. So much evidence has now been collected in support of this theory that no one any longer doubts that it is a truthful picture of things as they really are.

The kinetic-molecular theory of gases. The theory that was developed about the middle of the last century to account for the properties of gases is known as the kinetic-molecular theory. The essential postulates (assumptions) of this theory may be stated thus:

1. All gases are made up of extremely minute particles (molecules) which are relatively far apart in proportion to their diameters.
2. These molecules are in motion with great speeds.
3. The molecules are perfectly elastic, for there is no average loss of energy when one molecule collides with another or with the wall of the containing vessel.
4. A rise in temperature increases the kinetic energy of the moving molecules.

The ceaseless random motion, or thermal agitation, which these particles undergo is really *heat* itself, or rather the kinetic energy (motion energy) is heat. In terms of this heat-motion a great many effects of various sorts find their explanation. For instance, the tendency of a gas to spread, or *diffuse*, is to be attributed to the moving molecules, darting here and there. The molecules travel at high velocity, like bullets, in straight lines except when they strike the walls of the containing vessel or bump into one another and bounce off like billiard balls. The pressure of a gas against the containing walls is a gas-molecule bombardment of the walls, against which the molecules strike and then rebound. On the basis of the

assumptions just made as to the nature of a gas, we may now attempt to explain the gas laws.

Boyle's law. During the contraction of a gas produced by an outside pressure, the free space between the gas molecules is decreased. A contraction of the total gas volume to one half would squeeze the original number of molecules into half the original volume and would result in twice as many impacts in a given time upon the walls of the containing vessel. Consequently the pressure exerted by the gas would be double the original pressure. In an experiment of this sort the volume of the gas always decreases until the pressure exerted by the gas on the walls just balances the pressure applied from the outside.

Charles's law and Gay-Lussac's law. The kinetic energy of any moving particle is given by the expression $\frac{1}{2}mv^2$, in which m is the mass and v the velocity. Since experiment shows that mass is not altered by change of temperature, change in the kinetic energy of a molecule with change in temperature must come about by a change in the *velocity* with which it is moving. Thus, upon raising the temperature of a gas, the molecules strike the walls of the container more frequently and with greater impact. If the pressure on the gas is kept constant, the increased force of impact results in an expansion to a larger volume (Charles's law). On the other hand, if the volume is kept constant, this same increased impact increases the pressure exerted by the gas (Gay-Lussac's law).

Dalton's law. Since a gas is very largely made up of free space, it follows that in a mixture of gases the molecules of each type of gas are acting independently of the molecules of any other type. Hence the partial pressure exerted by a single gas is that which it would exert if it alone occupied the total volume.

Graham's law. While the molecules of a given gas do not all have the same velocity (some travel faster than others), and so do not all have the same kinetic energy, there is an *average velocity* and also an *average kinetic energy*. Maxwell has shown that for *any* two gases at the same temperature the average kinetic energy of the molecules of one gas is equal to the average kinetic energy of the molecules of the other. This is true *regardless* of how large or small the masses of the two different molecules may be.

$$\frac{1}{2} m_1 v_1^2 = \frac{1}{2} m_2 v_2^2 \quad (8)$$

If m_1 is small, v_1 must be relatively large; and if m_2 is large, v_2 is relatively small. Since the rate of diffusion depends on v , the velocity of the motion of the molecule, we have here stated the

essence of Graham's law; and if we solve the equation for v_1 and v_2 , we get Graham's law exactly:

$$\frac{v_1^2}{v_2^2} = \frac{m_2}{m_1}, \quad \text{or} \quad \frac{v_1}{v_2} = \frac{\sqrt{m_2}}{\sqrt{m_1}}$$

Graham's law: *The rate of diffusion is inversely proportional to the square root of the masses of the molecules, or the molecular weights.* This statement is equivalent to that given previously (p. 72): *The rate of diffusion is inversely proportional to the square root of the density of the gas.*

The scientific method. What we have been saying in the last few pages is a beautiful illustration of the application of the scientific method. Measurements of various sorts, during the past two or three hundred years, were made in connection with gases; thus facts were gathered, and this knowledge was organized and formulated in laws. Then a theory, the kinetic-molecular theory, was invented to explain the laws, and to give a plausible reason for the various ways in which gases behave. The theory was successful from the beginning, and was fortunate in having such masters as Rumford, Joule, Clausius, Maxwell, Kelvin, Boltzmann, Jeans, Langmuir, and others to nurse it along and develop it. The theory suggested further pioneering experimental work, and was itself gradually improved and strengthened until now it gives us a convincing and deeply satisfying insight into the nature of material particle behavior.

Avogadro's law. In 1811 the Italian Avogadro suggested what was known at that time as "Avogadro's hypothesis," namely, that *equal volumes of all kinds of gases at the same temperature and pressure contain the same number of molecules.* Avogadro proposed the idea originally to account for Gay-Lussac's law of combining gas volumes (a law of gas chemical behavior which will be discussed in Chapter 12), and also because it seemed reasonable to Avogadro to believe that equal volumes of gases, which contract in the same way under applied pressure and expand in the same way with rising temperature, would themselves be constructed in the same way and would almost certainly contain the same number of molecules. Avogadro's hypothesis was criticized and neglected for many years. But in 1860 Cannizzaro, another Italian, recalled the hypothesis to the attention of a congress of chemists and showed clearly, and to the satisfaction of most chemists of that time, that it was extremely plausible. Today Avogadro's hypothesis has been tested in so many different ways and verified so completely (within small limits of error) that we now call it *Avogadro's law*.

Avogadro's law and kinetic behavior. An individual gas molecule may be thought of as occupying, or darting around in, a certain volume of the gas space because of its kinetic energy, as it jostles and pushes back its neighbors. As the temperature drops, the kinetic energy is lowered, and the volume "claimed" (so to speak) by the molecule decreases. If the kinetic energy is increased, the volume per molecule increases. But Maxwell has shown that the average kinetic energy at a given temperature is the same for all different kinds of molecules, regardless of mass. Consequently we might expect different kinds of gas molecules to claim the same little average volume, approximately, and two crowds of different gas molecules in equal numbers at the same temperature and pressure to occupy the same total volumes.

GRAM-MOLECULAR VOLUME; EXPERIMENTAL DETERMINATION OF MOLECULAR WEIGHTS; COUNTING THE ATOMS AND MOLECULES

Introduction. We now come to a consideration of several things of the utmost importance in chemical theory and practice. Already, in Chapter 3, we have shown how the *atomic weights*, or relative weights of the atoms, can be measured by the positive-ray method; and in Chapter 4 we proved that the *gram-atomic weights* of all the different elements contain the *same number* of atoms. We said that this number is called the Avogadro number and that it is symbolized by the letter *N*. (At the end of this chapter we shall show how this number *N* can be counted.)

Gram-atomic volume of helium gas. Let us take the case of the element helium. The atomic weight of its atom, as determined by the positive-ray method, is 4.003 (referred to $O = 16$). Therefore its gram-atomic weight is 4.003 g; and if we weigh out, on a chemical balance, 4.003 g of helium we are weighing the Avogadro number, *N*, of helium atoms.

Now, since helium is a *gas*, let us fix our attention on the *volume* which 4.003 g of helium would occupy. The volume will depend, of course, on the temperature and pressure; but let us take standard conditions, 0° and 760 mm, and measure directly, in the laboratory, the volume of a gram-atomic weight of helium. This turns out to be 22.4 l, or 22,400 cc, and is appropriately called the *gram-atomic volume* of helium gas. The particles of helium gas have been shown to be single atoms; but some chemists, losing sight of our usual

distinction between an atom and a molecule, call the helium particles *molecules*, since they are the unit particles of the gas. In this sense we could speak of 22.4 l as being the *gram-molecular volume* of helium.

Gram-molecular volume. So far we have not described how the molecular weight of a true molecule, or cluster of atoms, can be determined. But in Chapter 3 we have shown in principle that the molecular weight is the sum of the atomic weights of the atoms present in the molecule. For example, the molecular weight of a

molecule of ammonia (NH_3) is $(14.008 + 3 \times 1.008) = 17.032$. In Chapter 4 we have proved that all gram-molecular weights contain the *same* number of molecules, and that this number is also the *same* as the number of atoms in a gram-atomic weight, namely, N , the Avogadro number. Or briefly:

Number of atoms in any gram-atomic weight (N) = number of molecules in any gram-molecular weight (N).

It therefore follows, from Avogadro's law, that a gram-molecular *volume* of ammonia gas (standard conditions) will also occupy 22.4 l, and that 22.4 l will be the gram-molecular volume for *all* gases.

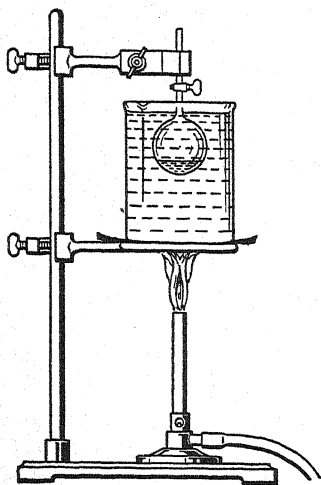


FIG. 49. *Method of Dumas*

Determination of molecular weights. We now find available for our use, in what we have just learned, a general method for determining molecular weights. The statement that "the gram-molecular weight of any gas occupies 22.4 l under standard conditions" can be turned around to read "22.4 l of any gas under standard conditions will contain the gram-molecular weight." We can therefore go into our laboratory, measure out a volume of 22.4 l of the gas in question, weigh it, and get the value for the gram-molecular weight and consequently also the molecular weight. Since 22.4 l is too large a volume to handle conveniently on the pan of a chemical balance, we may measure the weight of any convenient volume of the gas or vapor under any convenient conditions of temperature and pressure. Then we *calculate* the weight of 22.4 l under standard conditions.

Method of Dumas. This experimental method for determining vapor densities, employed as early as 1827 by the French chemist Dumas, is readily adapted to the present purpose. A glass bulb of

about 100 cc capacity is attached to a vacuum pump, exhausted of the air which it contains, and weighed empty. The flask is then filled with the gas under investigation, and again weighed. If we know the volume of the flask, the weight of the gas which fills it, and the temperature and pressure under which it was filled, it is easy to calculate the weight of 22.4 l of the gas under standard conditions. The method is also applicable to liquids that are easily vaporized. The liquid may be placed in the flask and the flask immersed in a bath the temperature of which is *above the boiling point* of the liquid (Fig. 49). The liquid rapidly boils away, drives out the air, and leaves the flask filled with the vapor of the liquid at the temperature of the bath and the pressure of the atmosphere. The flask may then be closed and its weight determined.

Examples. 1. Suppose that a Dumas bulb of 100 cc volume is filled with ammonia gas at 22° C and 745 mm, and that the ammonia is found to weigh 0.0688 g. What is the molecular weight of ammonia?

First, reduce the volume of the gas to standard conditions:

$$100 \text{ cc} \times \frac{745}{760} \times \frac{273}{295} = 90.7 \text{ cc}$$

Then $\frac{90.7 \text{ cc}}{22,400 \text{ cc}} = \frac{0.0688}{x}$; $x = 17$, the molecular weight

2. Let us place about 20 cc of *liquid* water inside a Dumas bulb of 100 cc volume, boil off the water, and finally bring the bulb to a temperature of 110° C in an oil bath just before we close off the bulb from the atmosphere (barometric reading is 752 mm). The weight of the water vapor is 0.0567 g. What is the molecular weight of water vapor?

Reduce the volume to standard conditions:

$$100 \text{ cc} \times \frac{752}{760} \times \frac{273}{383} = 70.5 \text{ cc}$$

Then $\frac{70.5 \text{ cc}}{22,400 \text{ cc}} = \frac{0.0567}{x}$; $x = 18$, the molecular weight

Deduction of the formula of a molecule. In the following table are listed the molecular weights of the gases hydrogen chloride, ammonia, methane, and water vapor, all determined by the Dumas method:

SUBSTANCE	MOLECULAR WEIGHT	FORMULA OF MOLECULE
Hydrogen chloride	36.5	HCl
Water	18	H ₂ O
Ammonia	17	NH ₃
Methane	16	CH ₄

The results by the Dumas method may be in error by a few per cent, but are accurate enough to allow us to deduce the formula for these molecules. Take methane, for example. The chemical decomposi-

tion of methane, by strong heating, yields carbon and hydrogen, and nothing else. Therefore only atoms of carbon and hydrogen are present in the molecule. Since the atomic weight of carbon is 12 (see

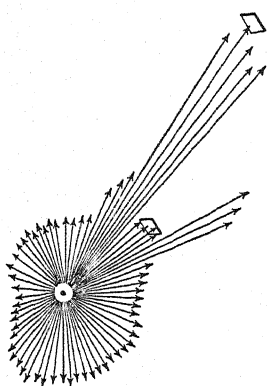


FIG. 50. *Diverging Alpha Particles and Two Zinc Sulfide Screens, the One Near and the Other Farther Away*

table on page 49), there can be only *one* atom of carbon in this molecule, and the rest of the molecular weight ($16 - 12 = 4$) must be contributed by hydrogen atoms. There must be *four* of these present, since the atomic weight of hydrogen is about 1. Therefore the formula for a methane molecule must be CH_4 .

By a similar argument, the formulas for the molecules of the other substances listed would be HCl , H_2O , and NH_3 . Later we shall present other methods for determining molecular weights, and describe a general procedure for deducing formulas, which involves not only the molecular weight but the percentage composition of the compound as determined by chemical analysis.

Counting the atoms and molecules. The student may remember that, in Chapter 3, we described the *spinthariscopes*, and said, "... a modified spinthariscopes has actually been used to count atoms." There are at least a dozen different methods that have been invented for counting or calculating the number of atoms or molecules in a given quantity of matter. We shall now describe the method that involves a slightly modified spinthariscopes, because it is probably the easiest method to understand.

Suppose that we have a spinthariscopes, with its zinc sulfide screen being bombarded by the alpha particles shot off from a piece of radium near by. If we try to count, through the magnifying glass, the tiny flashes of light, we find it is impossible to do so; there are *too many of them*. It is like trying to count the splashes of raindrops on a pond. But since the alpha particles (He^{++}) are shot out in all directions from the radium, and travel in straight lines, spreading radially (Fig. 50), if we could now place our zinc sulfide screen far enough away, we should find far fewer flashes of light appearing on

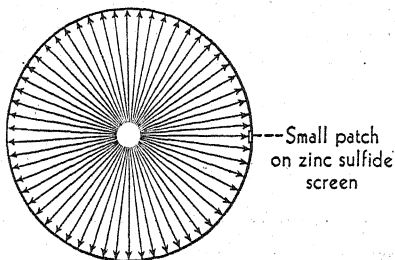


FIG. 51. *Large Spherical Shell*

it every second, and we might be able to count them. The only difficulty with doing this is the fact that the alpha particles will not travel very far through the air. They bump into thousands of air molecules along their path, and eventually are stopped short by the time they have traveled about 8 cm (about 3 in.). But we can easily overcome this difficulty by letting the little projectiles travel in a *vacuum*.

We might support the piece of radium at the center of a very large hollow spherical shell (Fig. 51), about 10 m (about 30 ft.) in radius, from which practically all the air has been pumped out, and count the flashes on a zinc sulfide screen covering the entire inside surface of the shell. But, of course, we should not actually try to count the flashes all over the shell, but select some very small fraction of the entire surface — for example, a patch of surface about $\frac{1}{100}$ as large as a dime or about as large as this letter "o."

If we thus chose a surface 1 mm² in area, trained a low-power microscope on it, and counted the flashes, we should get about 27 every second if we were using 1 g of radium 10 m away; if we chose 0.1 mm², we should get on the average 2.7; and we should not have any trouble counting 3 particles a second. Then, knowing the area of the whole large shell ($4\pi r^2$), we could easily calculate the *total* number of alpha particles shot out by 1 g of radium every second in *all* directions.

However, it would certainly not be an easy matter to construct such an enormous spherical shell. It would be about as large as the dome of a planetarium or an astronomical observatory. We could get exactly the same results by using the apparatus shown in Fig. 52. The radium is placed at one end of a long, evacuated glass tube. At the other end, 10 m away, is a small zinc sulfide screen *S* on a small patch of which our microscope is trained. Between the radium and the zinc sulfide are several metal plates *A*, *B*, *C* drilled with very tiny holes, which are all lined up like gun sights. Only the particles (leaving the radium) which are aimed directly at the patch on the zinc sulfide screen get there. All the many other particles, emitted in all other directions by the radium, and bouncing and ricocheting off the glass walls, do not get through the set of holes. With this arrangement, Rutherford and Geiger in 1915 showed that

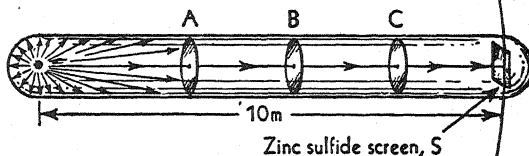


FIG. 52. Apparatus for Counting Alpha Particles

1 g of radium emits 34,000,000,000, or 3.4×10^{10} , alpha particles every second. If we multiply this number by the number of seconds in a year, which is about 32,000,000 (31,556,926), we find the number of alpha particles shot off by 1 g of radium in 1 year.

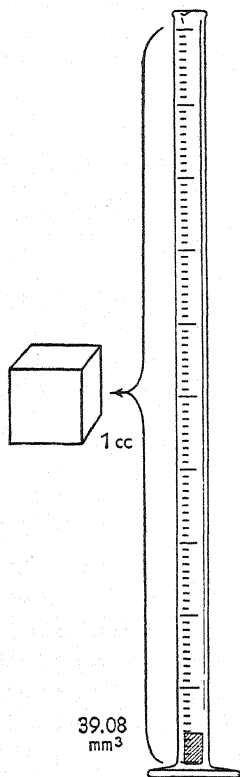


FIG. 53. Graduated Cylinder of 1 cc Volume. The Volume of 39.08 mm³ Is Indicated

Numerical value of N. An alpha particle is a helium ion, He^{++} . As every He^{++} comes off from the radium, it leaves its 2 electrons behind. But, very soon, all the electrons find their way back to the helium ions, which then become regular, neutral, helium atoms (or *molecules*, as some chemists call them). Thus, the long sealed glass tube of Fig. 52 gradually becomes filled with more and more helium gas. If we want to know how many particles are present in a given quantity of helium, all we have to do is to wait long enough for a sufficiently large quantity of the helium to accumulate so that we can collect it and measure its weight or its volume or both. Rutherford and Boltwood in 1915 showed that 1 g of radium in 1 year would produce about 39.08 mm³ of helium gas, measured at 0° and 760 mm (Fig. 53). This volume of helium gas would weigh about 0.00000698 g, or 6.98×10^{-6} g, not too small to be weighed on a sensitive microbalance.

Since we know the number of helium atoms, $31,556,926 \times 34,000,000,000$, present in 39.08 mm³ (or 0.03908 cc) and in 0.00000698 g, we can calculate the number of atoms in any volume or in any weight of helium that we please. Let us calculate (1) the number for a gram-molecular volume, namely 22.4 l (22,400 cc), and (2) for a gram-atomic weight (or a gram-molecular weight), namely 4.002 g.

$$\begin{aligned} (1) \quad \frac{0.03908 \text{ cc}}{22,400 \text{ cc}} &= \frac{3.2 \times 10^7 \times 3.4 \times 10^{10}}{x}; \\ (2) \quad \frac{6.98 \times 10^{-6} \text{ g}}{4.003 \text{ g}} &= \frac{3.2 \times 10^7 \times 3.4 \times 10^{10}}{x} \end{aligned}$$

The result is approximately 600,000,000,000,000,000,000, in both cases, or 6 followed by 23 ciphers (6×10^{23}). By another method,

the most accurate method we have for calculating this number, the value is 6.02×10^{23} . This is the value accepted today by physicists and chemists. It is probably in error no more than 1 in 1000.

This number, then, is the actual number for which our previous symbol N has been standing. This is the number of atoms in a gram-atomic weight of any element, the number of molecules in a gram-molecular weight of any compound, and the number of molecules in a gram-molecular volume of any gas. It is the *Avogadro number*. All atomic symbols and all molecular formulas mean two things to a chemist: (1) they stand for a single atom and a single molecule, and (2) they stand for 1 Avogadro number of atoms and 1 Avogadro number of molecules.

Questions

1. In science, what is the essential character of a *law*? of a *theory*?
2. In an encyclopedia read what you can find about the authors of the five laws explained in this chapter.
3. Since the atoms of different elements, and therefore the molecules of compounds made up of atoms, have very different volumes, how can it be that 22.4 l of *all* gases contain the same number of molecules?
4. In an experiment would it be possible to find that the volume of a gas, measured at a given temperature, had actually become smaller at a higher temperature?
5. Would the diffusion of a gas through the walls of a porous vessel be at the same rate as its escape through long capillary tubes?
6. What would be the effect of placing soft tennis balls in a vessel filled with hydrogen gas?

Problems

1. We have 1 l of gas at 0° and 760 mm. What would be the gas volume if (a) temperature were increased to 27° , at constant pressure? (b) temperature were decreased to -80° , at constant pressure? (c) pressure were increased to $3\frac{1}{2}$ atm, at constant temperature? (d) pressure were decreased to 600 mm, at constant temperature? (e) temperature were raised to 100° , and pressure lowered to 740 mm?
2. The inner tube of a certain automobile tire has a capacity of 1600 cu in. when inflated at 15° and under a pressure of 36 lb/sq in. Friction caused by rapid driving raised the temperature of the air in the tube to 110° . Calculate the increase in pressure within the tube (assuming that the volume of the tube has remained constant).

3. A student prepared 850 cc of oxygen, measured over water in a laboratory where the temperature was 25° and the barometer registered 750 mm. (a) What volume would this oxygen as dry gas occupy under standard conditions? (b) What would it weigh?

4. If the composition by volume of dry air is approximately 1 per cent argon, 21 per cent oxygen, and 78 per cent nitrogen, calculate by Dalton's law the partial pressure of each gas if the total pressure is 740 mm.

5. If 1 l of hydrogen will leak out (by diffusion) through a small hole in 1 hour, calculate the time for 1 l of the following gases to leak out under exactly similar conditions: oxygen, carbon dioxide, argon. (See the Appendix for the weight of 1 l of different gases.)

6. What volume of gas would contain one billion billion molecules under standard conditions?

7. How many molecules are there in an electric-light bulb of 200 cc volume at 25° and with pressure reduced by a vacuum pump to 1×10^{-6} mm?

8. In a Dumas bulb of 500 cc volume, water was heated at 130° until all excess was driven off and the bulb was filled with steam. When the bulb was sealed, the barometer read 750 mm, and the water vapor in the bulb weighed 0.2707 g. What is the molecular weight of steam?

Reading References

BRAGG. *Concerning the Nature of Things*. Chapter II (43 pages), "The Nature of Gases," is well worth reading.

BROWN. "Some Early Thermometers," *Journal of Chemical Education*, Vol. XI, pp. 448-453. This illustrates and explains the working of early thermometers based largely on the properties of gases.

DALTON, GAY-LUSSAC, and AVOGADRO. *Foundations of the Molecular Theory*, Alembic Club Reprints, No. 4.

LEONARD. *Crusaders of Chemistry*. Chapter V, entitled "The First Bishop of Science," tells the story of the life of Boyle and his discoveries.

MOORE. *History of Chemistry*. Chapter IV, "Boyle and His Contemporaries," will be found of interest.

WELCH. "The Kinetic Theory of Gases," *The Science Leaflet*, Vol. XI, pp. 457-461.

CHAPTER 6

Oxygen

Historical. Since we live at the bottom of a great sea of gases, about one fifth of which is oxygen, one might naturally suppose that this element would have been one of the first to be obtained in an approximately pure state and to be recognized as elementary in character. But the separation of a pure gas from the mixture that constitutes air was a task far beyond the ability of the early chemists. The first ones to get oxygen in anything like a pure condition did not get it from air, but from certain of its compounds.

Credit for the discovery of oxygen is given jointly to Joseph Priestley (Fig. 54), an English clergyman and investigator, and Scheele (Fig. 189), a Swedish chemist. Although Scheele actually prepared the gas a year earlier than Priestley, the major credit is given to the latter because he was the first to publish his results and describe the properties of the gas.

Priestley's discovery was made in 1774. In the course of some experiments with gases, or "airs" as he called them, it occurred to him to try the effect of heat upon certain solids in order to find out whether any gas is liberated by this means, and, if so, to collect the gas and to study its properties. Accordingly he floated the solids on mercury contained in a tube inverted over mercury, and heated them by focusing the sun's rays upon them by means of a large glass lens (Fig. 56). Among the solids so heated was the compound *mercuric oxide*. Collecting some of the gas which was given off, Priestley was surprised to find that a candle burned in it with a remarkably brilliant flame.

At the time of Priestley's discovery the renowned French chemist Lavoisier (Fig. 55) was engaged in a study of the mystery of "burning," and at once he became greatly interested in this newly discovered gas. He found that a number of elements such as phosphorus and sulfur burn in it to form compounds which were at that time regarded as acids. Believing that the characteristic properties of acids were due to the presence in them of this substance, he proposed the name *oxygen* for it, a word derived from the Greek and meaning "acid former." We now know that this name is not entirely appropriate, since many acids do not contain oxygen.

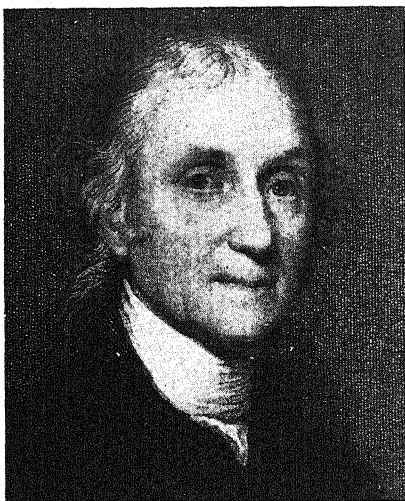


FIG. 54. *Joseph Priestley*
(1733–1804)

Distinguished English schoolteacher, philosopher, preacher, and scientist. The treatment he received because of his liberal religious views led to his emigration to the United States in 1794. He settled at Northumberland, Pennsylvania, where he continued his investigations until his death. The house in which he lived is preserved as a memorial to him. He isolated many important gaseous substances, including oxygen, hydrogen chloride, ammonia, carbon monoxide, nitric oxide, nitrous oxide, sulfur dioxide, and hydrogen sulfide



FIG. 55. *Antoine Laurent Lavoisier*
(1743–1794)

Distinguished French chemist, one of the greatest of all time. He demonstrated the true nature of combustion; introduced system into the naming and grouping of chemical substances; showed that bases and acids united to form salts; filled important positions in the French government; and was guillotined during the French Revolution because of his connection with the government

Occurrence. Among all the elements, oxygen easily stands first in order of abundance. It occurs in nature both in the free state and as a constituent of many compounds. In 100 volumes of dry air there are approximately 21 volumes of the free element. In the combined state it constitutes 88.81 per cent by weight of water and nearly one half by weight of the common minerals, such as limestone, sandstone, granite, and clay, which together make up the earth's crust. It is also an essential constituent of the compounds present in living organisms. For example, nearly two thirds of the human body is oxygen. The total weight of oxygen in the land, in the water, in the atmosphere, and in living organisms is roughly equal to the weights of all the other elements taken together.

Preparation. Since oxygen is so abundant and is present in such a great variety of compounds, it is easy to understand why many different methods may be used to obtain it in pure condition. The most important of these are the following:

1. *By heating certain compounds of oxygen.* Many compounds containing oxygen give off at least a portion of it when heated. For example, mercuric oxide (HgO) and potassium chlorate (KClO_3) — compounds which contain, respectively, 7.4 per cent and 39.2 per cent of oxygen — give off all their oxygen when heated to a moderately high temperature. Other compounds, such as manganese dioxide and barium peroxide, give up only a definite fraction of their oxygen.

2. *By the decomposition of water by means of an electric current.* Water is a compound, consisting of 88.81 per cent by weight of oxygen and 11.19 per cent hydrogen. If it contains a few drops of sulfuric acid, it is easily decomposed by an electric current (Fig. 57).

3. *By separation from air.* Since air contains such a large percentage of free oxygen, one would naturally expect methods to be devised for obtaining it from this source. The problem is not as simple as it may seem, for there are other gases in the air, and the separation of a gas in a pure condition from a mixture of gases is generally difficult. In this case it may be accomplished by a purely physical method as follows:

By subjecting air to the combined effects of high pressure and very low temperature it is possible to obtain it in the form of a liquid which is essentially a mixture of oxygen and nitrogen. If this liquid is allowed to stand under ordinary pressure, the nitrogen (since it is more volatile than the oxygen) rapidly vaporizes, leaving the oxygen as a moderately pure liquid, which in turn rapidly passes into the gaseous state.

Practical methods of preparation. With these general methods of preparation before us we may make a selection of those best suited to the actual preparation of the gas. For the purpose of

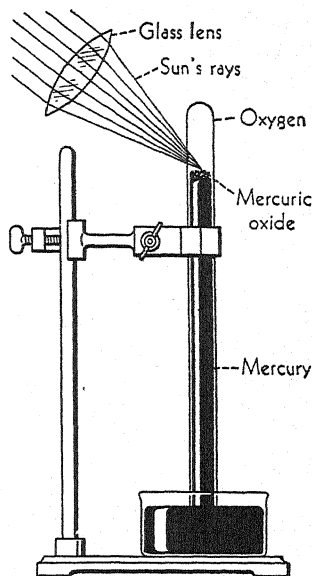


FIG. 56. Diagram of Apparatus to Illustrate Priestley's Method of Preparing Oxygen

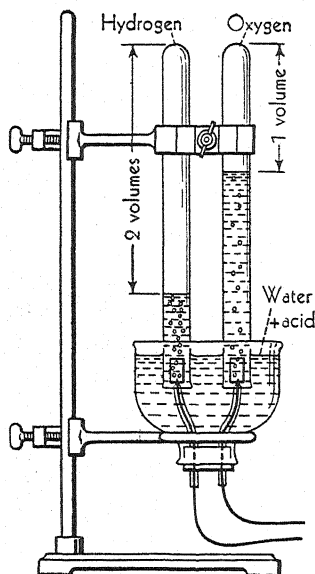


FIG. 57. *Diagram of Apparatus for Decomposing Water by the Electric Current*

laboratory experiments, in which relatively small quantities are desired, the choice will naturally be guided by convenience and simplicity of apparatus, while in the preparation on a commercial scale economy will determine the method.

Laboratory methods. 1. Preparation from potassium chlorate. The method usually chosen for preparing oxygen in the laboratory consists in heating potassium chlorate, which is a colorless solid and has the formula KClO_3 . The evolution of the gas becomes marked at about 400° ; and if the heating is continued long enough, all the oxygen present in the chlorate is liberated. It is a remarkable fact that the rate at which the oxygen is evolved at any given temperature is greatly increased by the presence of small quantities of certain substances, notably manganese dioxide. By mixing some manganese dioxide with the chlorate it is possible to liberate the oxygen rapidly at a much lower

temperature, namely, at about 200° .

Details of laboratory method. The operation, as carried out in the laboratory, is as follows: The potassium chlorate, mixed with about one fourth of its weight of manganese dioxide, is placed in a suitable vessel, such as a glass flask, which is provided with a stopper and glass tube, as shown at A (Fig. 58). By heating the mixture gently, oxygen is evolved and passes out through the tube B. It is evident that the oxygen at first escaping is mixed with the air contained in the flask. In a short time, as the evolution of oxygen continues, all this air is displaced, and the pure oxygen may then be collected by bringing the end of the delivery tube under the mouth of a glass cylinder C, which is inverted in a trough of water D. The oxygen gas, being lighter than water, collects in the cylinder, displacing the water.

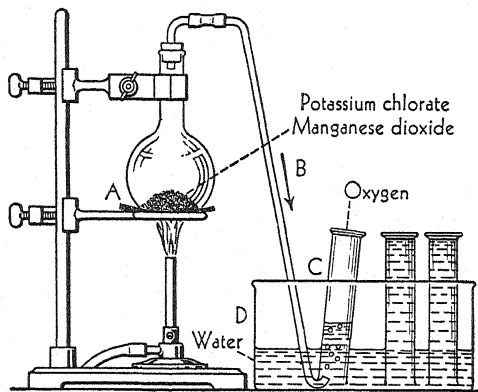
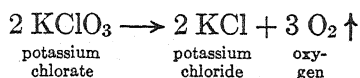


FIG. 58. *Diagram of Apparatus for Preparing Oxygen from Potassium Chlorate*

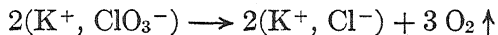
which has been filled with water and inverted in a trough of water *D*, as shown in the figure. The gas rises in the cylinder and displaces the water.

Characteristics of potassium chlorate. The composition of potassium chlorate (KClO_3) has been found to be as follows: potassium, 31.9 per cent; chlorine, 28.9 per cent; oxygen, 39.2 per cent. When the substance is heated, changes occur which finally result in the liberation of all the oxygen, while the potassium and chlorine remain in the form of a colorless solid compound known as potassium chloride (KCl). The fact that potassium chlorate yields potassium chloride and oxygen as the final products when heated may be expressed in the following way:



(A vertical arrow placed after the formula of an element or compound (see $3 \text{O}_2 \uparrow$ above) indicates that the substance is a gas and, under ordinary conditions, will be given off in that form.)

Potassium chlorate is really an electrovalent compound (K^+ , ClO_3^-) with a crystal lattice made up of the ions K^+ and ClO_3^- . The equation should be written,



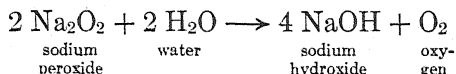
After the escape of the oxygen atoms (which double up to form oxygen molecules, O_2), the K^+ and Cl^- ions form crystals of potassium chloride.

Catalysts. As to the way in which the manganese dioxide promotes the decomposition of the potassium chlorate, it may be said at once that we do not know. Apparently it undergoes no permanent change during the reaction. Certainly it contributes no oxygen, for the weight of the latter obtained is always 39.2 per cent of the weight of the chlorate used, irrespective of the presence of manganese dioxide. This is but one example of many in which the rate of a chemical change is influenced by a foreign substance. Such a substance is called a *catalyst*, or a *catalytic agent*.

It is true that manganese dioxide gives up some of its oxygen when heated; but this requires a temperature above 400° , while the temperature reached in the preparation of oxygen from a mixture of potassium chlorate and manganese dioxide is only about 200° .

2. Preparation from sodium peroxide. A more convenient, although more expensive, method for preparing oxygen in the

laboratory consists in adding water to sodium peroxide. These two compounds, when brought into contact with each other, react in such a way as to liberate oxygen (Fig. 59). At the same time a colorless solid compound is formed, consisting of sodium, hydrogen, and oxygen, known as sodium hydroxide:



Commercial preparation. A number of methods for the preparation of oxygen on a large scale have been employed at different times.

In the United States, at the present time, nearly all the oxygen prepared for commercial purposes is obtained from liquid air; a small amount is prepared by the electrolysis of water. The gaseous oxygen is pumped into strong steel cylinders under great pressure and in this form is an article of commerce.

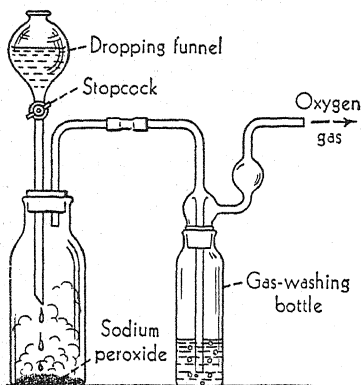


FIG. 59. Diagram of Apparatus Used for Preparing Oxygen by the Action of Water on Sodium Peroxide

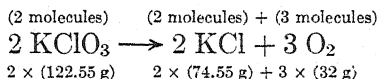
weighs 1.4290 g. Since 1 l of air under the same conditions weighs 1.2930 g, it will be seen that oxygen is 1.105 times as heavy as air.

To accomplish the liquefaction of oxygen the temperature must be at least as low as -118.8° , at which temperature a pressure of 49.7 atm. is required (see *critical temperature*, Chap. 8). At still lower temperatures less pressure will suffice. Liquid oxygen has a slightly bluish color and boils at -183° under a pressure of 1 atm. At its boiling point the liquid has a density of 1.14. By cooling this liquid to an extremely low temperature Dewar, an English investigator, succeeded in freezing it to a snowlike solid which melts at -218.4° .

Two atoms in the oxygen molecule. In the foregoing equations, we have represented oxygen not by its symbol alone, O, but by O_2 , indicating that the molecules of oxygen gas are composed of *two* atoms. What is the justification for doing this? In the chapter on

gases we saw how one could determine the *approximate* molecular weight of a gas or readily volatilized liquid by obtaining the weight of a definite volume of the gas or vapor, correcting to standard conditions, and calculating the weight of 22.4 l. Approximately this volume, at 0° and 760 mm, contains a gram-molecular weight, or N (Avogadro's number) of gas molecules. We have just stated that 1 l of oxygen gas under standard conditions weighs 1.4290 g; and 22.4×1.4290 is 32.0096 (the approximate molecular weight). Since the atomic weight of oxygen is exactly 16.000, it follows that there are 2 atoms of oxygen in a molecule.

Volume of oxygen gas furnished by a given weight of potassium chlorate. Toward the end of Chapter 4 we showed how the information contained in an equation representing a chemical reaction might be used to calculate reacting quantities, or the weights of reactants required to yield a desired weight of product. For example, the equation

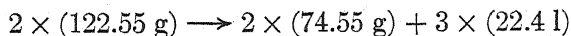


tells us the number of molecules and the number of gram-molecular weights (indicated above and below the symbols in the equation; see table of atomic weights, p. 49). Consequently, if we wish to know how many grams of oxygen may be obtained from 100 g of potassium chlorate, we need only set up the proportion

$$\frac{245.10 \text{ g potassium chlorate}}{100 \text{ g potassium chlorate}} = \frac{96 \text{ g oxygen}}{x \text{ g oxygen}}$$

and solve for x . Thus x is found to be 39.16 g, which is the weight of oxygen gas yielded by the complete thermal decomposition of 100 g of potassium chlorate.

Moreover, the same equation yields still further information. Since oxygen is a gas, the three gram-molecular weights will occupy three gram-molecular volumes, $3 \times (22.4 \text{ l})$, at standard conditions.



Hence, if we wish to know the volume of oxygen (measured at standard conditions) which may be generated from 10 g of potassium chlorate, we set up the proportion

$$\frac{245.10 \text{ g potassium chlorate}}{10 \text{ g potassium chlorate}} = \frac{67.2 \text{ l oxygen}}{x \text{ l oxygen}}$$

Solving for x , we find that 2.74 l of oxygen will be formed.

Laboratory corrections. In the laboratory it is not likely that we would collect oxygen at standard conditions. Suppose that the temperature of the laboratory is 22° , that the barometric pressure is 750 mm, and that the oxygen is collected over water. Under these conditions the oxygen would occupy not 2.74 l but a different volume, which may be calculated from the gas laws.

$$V = 2.74 \times \frac{760}{(750 - 19.83)} \times \frac{(273 + 22)}{273}$$

This volume is found to be 3.08 l.

Chemical conduct. At ordinary temperatures oxygen is only a moderately active element — a fact which may be inferred from our experience that very few of the materials coming under common observation are acted upon by the oxygen of the air with noticeable rapidity. With rise of temperature it rapidly becomes more active. At ordinary temperatures, for example, the elements sulfur, iron, and carbon are not visibly acted upon by oxygen, while in the case of phosphorus the action, though slow, is quite apparent. If now the temperature of each of these elements is slowly raised, the reaction becomes more marked, and the phosphorus soon bursts into flame. At higher temperatures the sulfur, carbon, and iron are likewise ignited. If each of these elements, as soon as ignited in the air, is introduced into a vessel of pure oxygen

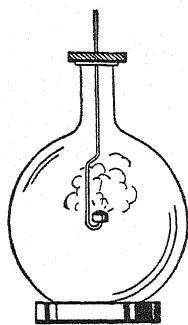


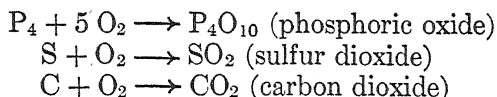
Fig. 60. *Burning Sulfur in Oxygen*

(Fig. 60), the action becomes much more energetic. The pale-blue flame of the burning sulfur is greatly increased in size and brightness, the iron throws off countless sparks, while the phosphorus and carbon burn with dazzling brilliancy. In each case the action increases in intensity as it progresses. Many compounds act in the same general way. Thus, wood, coal, oil, fats, and fuel gases all burn readily in air and more brilliantly in pure oxygen. It was a brilliant candle flame that led Priestley to the discovery of oxygen (p. 85). Indeed, there are but few, if any, elements which will act upon so many other elements and compounds as does oxygen.

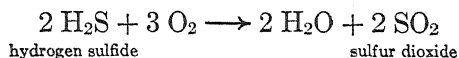
This general conduct suggests a great many questions. What becomes of the substances when they burn? Why is there a difference in the ease of ignition? Why do not all substances burn? Why is the action more intense in oxygen than in the air, and why does it become more energetic and brilliant as it progresses? Some

of these questions can be answered at once; others will occur again many times in our study, and in the end will remain only partially answered.

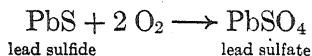
The nature of the action of oxygen upon substances; oxidation; oxidizing agent. Experiments have shown that the action of oxygen upon another element consists in the union of the two elements to form a compound. Thus, for the burning of phosphorus, sulfur, and carbon, we may represent the reactions by the following equations:



The action of oxygen upon compounds is similar to its action upon elements, and usually consists in the union of oxygen with one or more of the elements present in the compound. Thus, when the gaseous compound of hydrogen and sulfur known as *hydrogen sulfide* burns in air or in oxygen, both the hydrogen and the sulfur combine with the oxygen:



In some cases the compound as a whole unites with the oxygen:



When any substance (or its constituent parts) combines with oxygen, the substance is said to be *oxidized*, and the process or change which takes place is called *oxidation*. Thus, we say that phosphorus is readily *oxidized* or that it easily undergoes oxidation. Oxidation may be brought about by the use of oxygen or of some compound that will readily supply oxygen, such as potassium chlorate or sodium peroxide. When so used, the oxygen itself or the compound which furnishes the oxygen is called the *oxidizing agent*.

It will be pointed out in the appropriate place that the use of the term *oxidation* is not limited to such changes as those mentioned above but has a much broader application, embracing a large group of reactions, in many of which no oxygen takes part. For the present, however, the term will be used in the sense explained above.

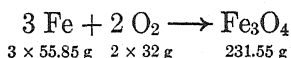
Oxides; products of oxidation. When any element combines with oxygen, the resulting compound is known as an *oxide* of that element, as indicated by the parenthetical names in the equations

given above. An oxide is any compound composed of two elements, one of which is oxygen. The particular oxide or oxides formed in the oxidation of any substance are known in general as the *products of oxidation* of that substance.

Most of the elements form oxides; indeed, some of the elements form more than one oxide, as is the case with carbon, which forms carbon monoxide (CO) and carbon dioxide (CO₂). Some of the oxides are invisible gases, as is true of the oxides of sulfur and carbon, formed when these two elements burn in air or in pure oxygen. In a few cases the oxide is a liquid, the most familiar example being water, which is an oxide of hydrogen. In the great majority of cases, however, the oxides are solids.

Weight relations in oxidation. Since oxidation is essentially the union of oxygen with other elements or compounds, it must follow that the weight of the product formed is greater than that of the substance oxidized or burned.

The equations which we have written for oxidation processes express the same conclusion. In the case of iron the weight relationships are



This gain in weight may be demonstrated by weighing some powdered iron in a porcelain crucible (Fig. 61), heating the open crucible and its contents in a hot flame, and then reweighing. The increase in weight represents the oxygen which has combined with the iron.

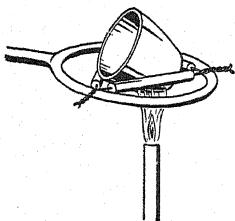


FIG. 61. *Heating Iron in an Open Crucible*

Our common experience with fuels would hardly lead us to such a conclusion, because the ash remaining after burning represents only a small fraction of the total weight of fuel consumed. But, of course, the products of ordinary combustion, largely water and oxides of carbon, are volatile and escape up the chimney. Experiments may be performed in which these gaseous products are collected and weighed. Here, as in all other cases, it can be shown that the weight of the substance oxidized, plus that of the oxygen used up, exactly equals the weight of the products of the oxidation.

Exothermic and endothermic reactions. When such a substance as iron, carbon, sulfur, or phosphorus burns in oxygen, heat is evolved, the exact amount depending upon the nature and the weight

of the substance. Thus, when carbon burns in oxygen, 7858 cal are liberated for each gram of carbon burned, while under similar conditions 1 g of sulfur will liberate 2161 cal. All such reactions in which heat is liberated are known as *exothermic reactions*.

In many other reactions heat is absorbed and it must be supplied from some external source if the chemical action is to continue. Thus, if we wish to decompose mercuric oxide into the elements mercury and oxygen, we must apply heat continuously; otherwise the reaction will cease. For example, to decompose 1 g of mercuric oxide requires 104 cal. Moreover, the heat which is applied must be above a certain intensity, or temperature. This heat is stored up as chemical energy in the resulting mercury and oxygen. All such reactions which take place only with absorption of heat are known as *endothermic reactions*.

In line with these same terms, an *exothermic compound* is one that evolves heat as it is formed, while an *endothermic compound* is one that absorbs heat during its formation.

Heat, temperature, and light in oxidation; combustion. In the oxidation of the elements that we have been considering, the rate of oxidation may at first be quite slow, with little heat given out and no light. If the conditions are such that the loss of heat by radiation and conduction is small, the major portion of the accumulating heat serves to raise the temperature of the materials involved in the reaction. As the oxidation proceeds, the temperature may rise rapidly, and light may appear, in some cases becoming almost blinding. The higher the temperature, the larger is the fraction of heat converted into visible radiant energy (light). Increasing brightness is therefore an indication of rising temperature.

Such a reaction is called a *combustion*. Although this term is often used as a synonym for *oxidation*, it is usually reserved for those chemical reactions which are accompanied by the evolution of heat and light. The most familiar examples of combustion are those in which substances "burn" in air or oxygen, but in subsequent pages we shall meet with cases of combustion in which no oxygen takes part in the reaction.

Kindling temperature and spontaneous combustion. Before any substance will undergo self-sustaining combustion its temperature must be raised to a definite point known as its *kindling temperature*. This temperature varies from substance to substance and also with the reaction conditions for the same substance. Thus, the kindling temperature of phosphorus is very low, while that of iron is much higher.

Materials taking fire on their own account, without the application of a flame or spark, are said to undergo *spontaneous combustion*. It will be seen that the essential conditions are (1) an existing slow oxidation and (2) good heat insulation.

Illustrations. Linseed oil, used in paints, may attain rather rapid oxidation in air, and oily rags left by painters not infrequently occasion disastrous fires. Fine coal in the center of a heap or in the closed hold of a vessel sometimes takes fire. Almost any finely divided combustible material, such as sawdust or flour, is dangerous when stored in a warm, dry place. Sometimes the heat of fermentation, which is a kind of oxidation, will start a fire in a haystack or a barn if the hay is not well dried before being stored.

Incombustible substances. The question naturally rises, Why do not all substances burn? In the case of many substances, such as the compounds formed in combustion, the answer is very evident, for they already contain all the oxygen with which they are capable of uniting. Many oxides, such as water, are of this class, as well as most of the substances which constitute the solid crust of the earth. The materials of which fireproof buildings are made — brick, tile, cement, plaster, asbestos — are also of this character. Some of the metals, like iron, will burn, but only at such high temperatures that they are practically incombustible unless they are in a finely powdered form. Other substances, however, such as the elements helium and argon, do not combine with oxygen under any known condition.

Speed of chemical reactions. The description of the conditions which lead to spontaneous combustion, and also the description of the course of the decomposition of potassium chlorate, have made it clear that a given chemical reaction may take place at different rates under different conditions. We recognize four important factors which control the velocity of chemical reactions in general.

1. The *nature* of the reacting substances is of prime importance.

Once we have chosen the reacting substances for a given reaction, it is true that

2. The *temperature* is extremely important; the higher the temperature, the faster the reaction.

3. Increasing the *concentration* causes the reaction to increase in velocity; the same result is achieved with gases by increase of pressure, and with solids by increasing the degree of subdivision or the amount of surface exposed to attack.

4. The presence of a *catalyst* modifies the rate profoundly.

All these factors will be treated in more detail in Chapter 19.

Importance of oxygen. The great importance of oxygen in nature is evident from the facts which have already been presented in this chapter. It is a constituent of the great majority of the compounds which collectively constitute the solid earth, the living creatures upon it, and the water which covers so much of its surface, while the atmosphere is a great reservoir from which a supply of the free element can be drawn at any time.

Free oxygen is essential to the life of all organisms, with the exception of some of the lowest microscopic forms. Aquatic animals obtain the necessary oxygen from the air dissolved in the water in which they live. In animals the oxygen inhaled into the lungs is absorbed by the blood and carried throughout the body; it enters into the cells composing the tissues, and oxidizes old tissues and food materials; these oxidations maintain the temperature of the body. Free oxygen also plays a prominent part in the decomposition of refuse matter which collects on the surface of the earth, much of it being oxidized into harmless gases. Sewage is purified by spraying it into the air so that oxygen can come in contact with the noxious materials and oxidize them. It is noteworthy, however, that the oxidation of such matter takes place only in the presence of certain forms of minute living organisms known as *bacteria*.

Commercial uses of oxygen. Enormous quantities of oxygen from 95 to 100 per cent pure are now prepared from liquid air for commercial uses. By far the greater part of commercial oxygen is used in the production of high temperatures (see oxyacetylene blowpipe) for the cutting and welding of metals. Smaller amounts are used for the treatment of those diseases (such as pneumonia) in which the patient is unable to inhale sufficient air to supply the necessary quantities of oxygen. Aviators are supplied with the pure gas for use at high altitudes, and miners inhale it when entering mines after an explosion. It is of interest to note that pure oxygen may be inhaled for a number of hours apparently without injurious effects.

OZONE

Introduction. When electric sparks are passed through oxygen, it acquires a peculiar odor. The oxygen so treated imparts a blue color to strips of paper which have been dipped into a solution of potassium iodide and starch. Evidently a new substance is present which, unlike oxygen, is capable of liberating iodine, which in turn forms a blue compound with the starch. Schönbein called this new substance, formed in the oxygen, *ozone* (meaning "to smell").

Preparation. Ozone is usually prepared by passing oxygen between plates that are highly charged electrically (which gives the so-called silent discharge); in this way the heating effect of a spark discharge is avoided (Fig. 62).

To obtain the greatest yield the oxygen should be cold and free from moisture. Under ordinary conditions 5–10 per cent of the oxygen is converted into ozone. At lower temperatures a larger yield may be obtained, reaching 90 per cent at the temperature of liquid air. To prepare pure ozone the mixture of oxygen and ozone is cooled with liquid air. The ozone, being much more readily condensed than oxygen, is obtained in a liquid state almost free from oxygen.

Ozone is formed in small percentages in reactions in which oxygen is liberated at low temperatures, as in the decomposition of water by the electric current. It is also produced in some oxidations, as when moist phosphorus slowly oxidizes in air.

Properties and conduct. Ozone is a gas of pale-blue color and characteristic odor. It is 1.5 times as heavy as oxygen, since 1 l of the gas weighs 2.144 g. The density of ozone gives us the clue to

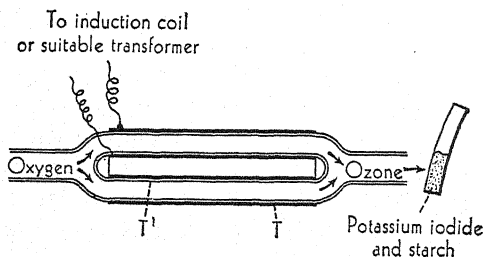


FIG. 62. *Diagram of Apparatus Used for Preparing Ozone by the Action of the Electric Discharge on Oxygen*

the manner in which it differs from ordinary oxygen. Since ozone is formed from oxygen alone, ozone must be elementary in character. Moreover, its molecular weight is 48 (that is, 22.4×2.144), which indicates that the molecule of ozone consists of 3 atoms ($\frac{48}{16}$) of oxygen. Thus we write O_2 for ordinary oxygen and O_3 for ozone.

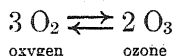
When cooled sufficiently, ozone condenses to an indigo-blue liquid which boils at -112° . Ozone resembles oxygen in its chemical conduct but is much more active and is therefore a very powerful oxidizing agent. Such metals as silver and mercury, which are not easily acted upon by oxygen, quickly tarnish in air containing ozone. It oxidizes many organic dyes, forming colorless compounds, and so acts as a bleaching agent. When pure it is a dangerous explosive, owing to its spontaneous conversion into oxygen.

In view of its great activity it is doubtful whether ozone is ever present in the air near the earth's surface in appreciable quantities. It is doubtless

formed during lightning discharge, but it must very speedily disappear through chemical action upon oxidizable materials which are always present. The air collected on high mountaintops, however, is said to contain recognizable percentages of ozone. Certain facts have led to the conclusion that a small concentration of the gas exists in the upper region of the atmosphere, where it is formed by the action of ultraviolet light.

Uses of ozone. Ozone has certain commercial applications, all based on its strong oxidizing properties. Thus it is used as a bleaching agent, as a disinfectant, as a deodorizer, and as an oxidizing agent in the preparation of a number of useful products. It is also being used in Europe for the sterilization of drinking waters. The substance employed for these various purposes is not pure ozone but ozonized air, which is prepared as it is needed.

The conversion of oxygen into ozone reversible. The reason why only a relatively small percentage of the oxygen subjected to an electric discharge is transformed into ozone is that under all ordinary conditions ozone changes back into oxygen. These two opposite changes may be represented as follows, the arrows indicating the direction in which each change proceeds :



When the speed with which the oxygen changes into ozone exactly equals the speed with which the resulting ozone changes back into oxygen, the two substances are said to be in a *state of equilibrium*. The percentage of ozone present when equilibrium is reached is clearly the maximum yield under the conditions of the experiment. Such reactions as the above are termed *reversible reactions*.

The difference between oxygen and ozone. Ozone differs from oxygen not only in the composition of its molecules but also in its energy content. In the transformation of oxygen into ozone by the usual method electrical energy is absorbed. When ozone spontaneously changes into oxygen, about 717 cal of heat is liberated for each gram so changed ; and when it acts as an oxidizing agent, the heat evolved is correspondingly greater than when the same oxidation is accomplished by oxygen.

Questions

1. Oxygen is a moderately active element. Why should there be so large a percentage of free oxygen in the air?
2. Since oxygen is heavier than the nitrogen of the air, why does not the oxygen settle out as a heavier layer at the surface of the earth?

3. Air and water cost nothing and both are possible sources of free oxygen. Why is commercial oxygen made from air rather than from water?

4. Both potassium chlorate and manganese dioxide contain oxygen. When a mixture of the two is heated, oxygen is evolved. How would you prove whether the oxygen comes from the chlorate, from the dioxide, or from both?

5. Do we add manganese dioxide to potassium chlorate (a) to obtain more oxygen or (b) to set free the oxygen at a lower temperature or (c) to set free the oxygen more rapidly at a given temperature?

6. Why do we not think of ozone as an element different from oxygen?

7. Why does pouring water on a burning building check the speed of the fire?

8. We have to heat charcoal in air to get it to burn, and we must heat mercuric oxide to decompose it. Why do we call the one reaction exothermic and the other endothermic?

Problems*

1. Mercuric oxide, potassium chlorate, and water contain respectively 7.4, 39.2, and 88.81 per cent of oxygen by weight. Calculate the weight of each of these compounds that would yield 100 l of oxygen.

2. In the preparation of oxygen by heating a mixture of 10 g of potassium chlorate and 4 g of manganese dioxide, (a) what volume of oxygen would be obtained? (b) What compounds would remain in the flask? (c) What would be the weight of each of these?

3. Commercially pure potassium chlorate costs about 60 cents per kilogram and mercuric oxide \$4.50 per kilogram. What volume of oxygen could you obtain from one dollar's worth of each of these compounds?

4. By the method on page 91, calculate the volume of oxygen (over water), at 25° and 745 mm, that can be obtained from 2 g-mol. wt of H_2O by electrolysis.

Reading References

FARADAY. *Chemical History of a Candle*. A classic treatise intended for juveniles, but mature students will read it with interest.

FOSTER. *The Romance of Chemistry*. Chapter V is entitled "Oxygen. Fire and Flame."

GOLDSCHMIDT and others. A number of papers dealing with the life and work of Priestley, *Journal of Chemical Education*, Vol. IV, pp. 145-199. Very interesting and well illustrated.

*In all problems throughout the text, gases are supposed to be measured under standard conditions unless otherwise specified.

JAFFE. *Crucibles*. Chapter IV, on Priestley, and Chapter VI, on Lavoisier, are well worth reading.

LEONARD. *Crusaders of Chemistry*. Chapter VI, entitled "The Chemical Revolution," gives an account of the phlogiston theory. Chapter VII gives interesting events in the life of Priestley, while Chapter IX, in a similar way, treats the life of Lavoisier.

MOORE. *History of Chemistry*. Chapter V tells of Priestley and Scheele in relation to the discovery of oxygen. Chapter VI gives a brief account of Lavoisier and his work on combustion.

PRIESTLEY and SCHEELE. *Alembic Club Reprints*. No. 7, by Priestley, and No. 8, by Scheele, tell of the discovery of oxygen.

WEEKS. *The Discovery of the Elements*. Pages 35-48 tell of the discovery of oxygen.

WORSTELL. "On Ozone," *Journal of Chemical Education*, Vol. IX, pp. 291-300.

The magazine *Fortune*, Vol. XVI, No. 2, p. 61, treats of oxygen in an interesting way.

CHAPTER 7

Hydrogen

Historical. Since hydrogen is easily prepared by the action of sulfuric acid on iron, and since these two substances have long been known, it seems certain that the alchemists must have been somewhat familiar with this gas. Paracelsus (1493-1541) states that when sulfuric acid and iron are brought together, "an air arises which bursts forth like the wind." However, the English investigator Cavendish



FIG. 63. Henry Cavendish
(1731-1810)

A famous English scientist, contemporary with Joseph Priestley. He described hydrogen as a new gas, and showed that it produced water when burned

which bursts forth like the wind." However, the English investigator Cavendish (Fig. 63) is usually regarded as the discoverer of hydrogen because he was the first to get it in pure condition (1766) and to recognize it as an independent substance different from other known inflammable gases. Cavendish called the gas *inflammable* air, but later, when the gas was found to be a constituent of water, Lavoisier renamed it *hydrogen*, meaning "water former."

Occurrence. In the free condition hydrogen is sometimes found in gases issuing from the earth in volcanic regions. It is also said to be found in the atmosphere to the extent of about 1 volume in 10,000 of air, though it seems probable that the relative percentage is much greater in the upper regions of the atmosphere. The spectroscope reveals huge quantities of the free element in the gases surrounding the sun and certain other stars. Combined with oxygen in the form of *water* it is widely distributed.

Combined with carbon it forms a large number of important compounds known as *hydrocarbons*, which constitute by far the greater part of *natural gas* and *petroleum*. It is likewise a constituent of the compounds present in living organisms and of most of the products derived from them, such as sugar, starch, fat, and protein.

Laboratory preparation of hydrogen. Since hydrogen is not found in the free condition to any appreciable extent, it must be prepared from its compounds. The ones most often used as sources of hydrogen are (1) *water*, (2) *acids*, and (3) *bases*.

1. Preparation from water. Hydrogen may be liberated from water by two general methods: (a) by the action of the electric current, as described under the methods for the preparation of oxygen (Fig. 57); (b) by the action of certain metals. A few metals, such as sodium, potassium, and calcium, act rapidly upon water even at ordinary temperatures, liberating one half of the hydrogen present in the water acted on (Fig. 64). The remainder of the hydrogen, together with all the oxygen, combines with the metal to form compounds known as hydroxides. We may represent the reaction between sodium and water as follows:

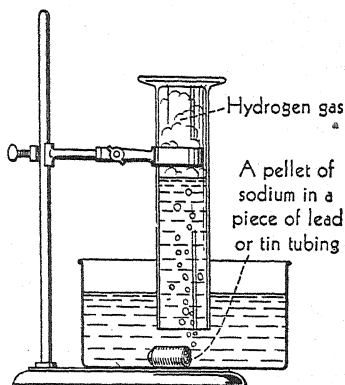
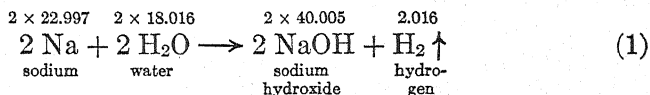
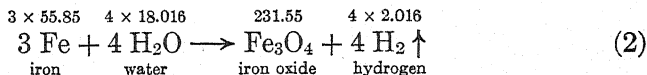


FIG. 64. Diagram Illustrating the Method of Preparing Hydrogen by the Action of Water on Sodium



Other metals, such as magnesium and iron, also decompose water rapidly, but only at high temperatures. In such cases the decomposition is best effected by heating the metal to redness in a tube of iron or porcelain and then passing steam over the red-hot metal. Under these conditions the metal combines with the oxygen of the water to form an oxide, while the hydrogen is liberated (Fig. 65). For example, in the case of iron the reaction may be represented as follows:



2. Preparation from acids. The *acids* are an important class of compounds containing hydrogen, which is liberated when the acid is brought into contact with certain metals. This reaction suggests a simple and convenient method for preparing hydrogen in the laboratory. Usually *zinc* or *iron* is used. The acid commonly employed is either *hydrochloric acid* or *sulfuric acid*. Hydrochloric acid is an

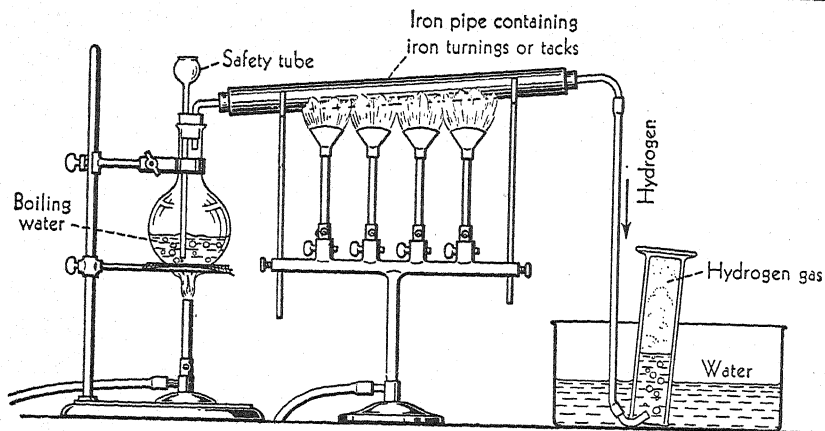


FIG. 65. Diagram Illustrating the Method of Preparing Hydrogen by the Action of Steam on Iron

aqueous solution of a gaseous compound called *hydrogen chloride* (HCl), while *sulfuric acid* is an aqueous solution of an oily liquid known as *hydrogen sulfate* (H_2SO_4). To liberate hydrogen from these acids it is only necessary to bring the acid, properly diluted with water, into contact with the metal. The metal gradually passes into solution, while the hydrogen of the acid is in turn set free (Fig. 66). The liberation of the hydrogen is indicated by the bubbles rising in the liquid. When zinc and sulfuric acid are used in the preparation, the reaction may be represented in a general way as follows:

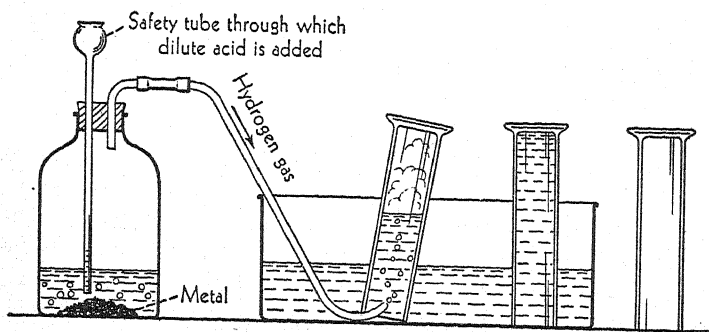
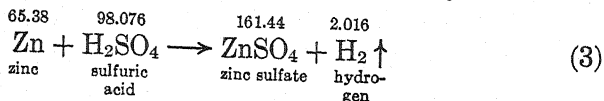
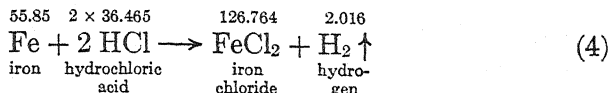


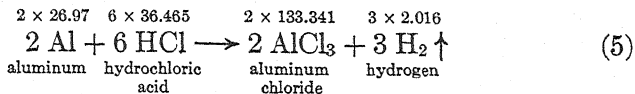
FIG. 66. Diagram of Apparatus Used for Preparing Hydrogen by the Action of an Acid on a Metal

It will be noted that the zinc simply takes the place of the hydrogen in the acid. The resulting compound of zinc, sulfur, and oxygen, known as zinc sulfate, is a colorless solid which remains dissolved in the excess water and may be obtained by evaporating the solution.

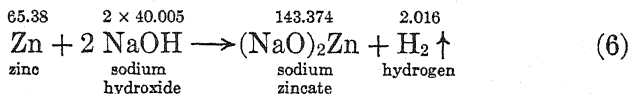
When iron and hydrochloric acid are used in the preparation of hydrogen, the reaction may be represented as follows:



Aluminum reacts with hydrochloric acid as follows:



3. Preparation from bases. The bases are compounds of a metal with oxygen and hydrogen. Certain metals, such as zinc and aluminum, react with some of the bases, especially sodium hydroxide (NaOH), liberating the hydrogen present in them.



Equivalent weight and valence. In the reactions in which metals displace hydrogen from its compounds, as shown in the equations (1), (3), (4), (5), and (6) of the last few pages, it will be noted that

1 g-at. wt of sodium (Na) $\frac{22.997 \text{ g}}{1 \text{ g-at. wt}}$ displaces 1 g-at. wt of hydrogen (H) or $\frac{1}{2}$ g-mol. wt ($\frac{1}{2} \text{H}_2$) $\frac{1.008 \text{ g}}{1 \text{ g-mol. wt}}$

1 g-at. wt of $\left\{ \begin{array}{l} \text{zinc (Zn)} \\ \text{or iron (Fe)} \end{array} \right\}$ $\left\{ \begin{array}{l} 65.38 \text{ g} \\ 55.85 \text{ g} \end{array} \right\}$ displaces 2 g-at. wt of hydrogen (2H) or 1 g-mol. wt (H_2) $\left\{ \begin{array}{l} 2 \times 1.008 \text{ g} \\ 2.016 \text{ g} \end{array} \right\}$

1 g-at. wt of aluminum (Al) $\frac{26.97 \text{ g}}{1 \text{ g-at. wt}}$ displaces 3 g-at. wt of hydrogen (3H) or $1\frac{1}{2}$ g-mol. wt ($1\frac{1}{2} \text{H}_2$) $\frac{3 \times 1.008 \text{ g}}{1.5 \text{ g-mol. wt}}$

We should therefore expect the volumes of hydrogen gas (at standard conditions) liberated by gram-atomic weights of sodium, zinc (or iron), and aluminum, respectively, to be in the ratio of 1:2:3. This is indeed found to be true (Fig. 67).

In other words, 1 g-at. wt of hydrogen (1.008 g) is displaced by 22.997 g sodium, by $\frac{1}{2} \times 65.38 \text{ g}$ zinc (32.69 g), by $\frac{1}{2} \times 55.85 \text{ g}$ iron (27.925 g), by $\frac{1}{3} \times 26.97 \text{ g}$ aluminum (8.99 g). The *weight* (in grams) of an element which will displace or combine with 1 g-at. wt of

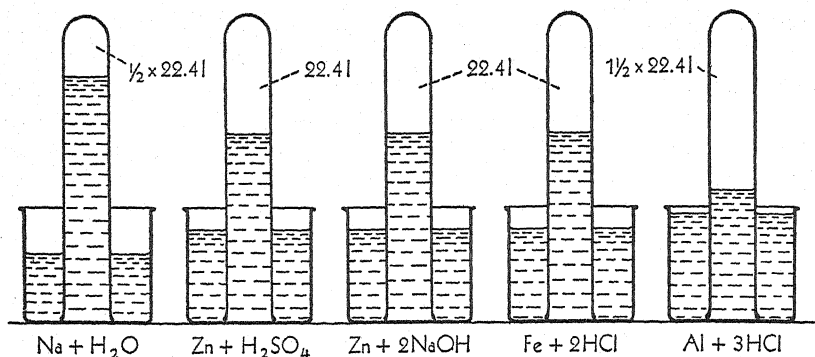
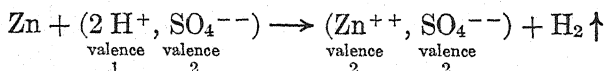


FIG. 67. Diagram Showing Volumes of Hydrogen Liberated by the Gram-Atomic Weights of Four Metals

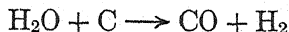
hydrogen is called the *equivalent weight* (or combining weight) of that element.

Valence is a number, as already indicated (p. 43). It is the number of gram-atomic weights of hydrogen which the gram-atomic weight of an element will displace or combine with. Thus the valence of sodium is 1, of zinc 2, of aluminum 3. The valence may be found by dividing the gram-atomic weight by the equivalent weight; for zinc it is $65.38 \div 32.69 = 2$. The valence of these metals may also be stated as the number of charges carried by the ions of the metals, Na^+ , Zn^{++} , Fe^{++} , Al^{+++} . Since the hydrogen ion itself carries only one charge, H^+ , it is clear why a zinc ion, for example, will take the place of two hydrogen ions:

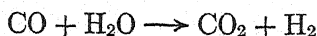


Commercial methods for the preparation of hydrogen. A number of methods are employed in preparing hydrogen on a large scale for commercial uses.

1. The principal method, known sometimes as the *Bosch process*, consists in passing steam over highly heated carbon in the presence of a suitable catalyst. Carbon monoxide (CO) and hydrogen are first formed as shown in the following equation:

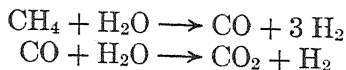


The resulting carbon monoxide then reacts with the steam, forming carbon dioxide (CO_2) and hydrogen:



The carbon dioxide is separated from the hydrogen by passing the mixture through water under pressure; the carbon dioxide dissolves in the water and leaves the hydrogen pure or nearly so.

2. A second important process consists in the action of steam on methane (CH_4), a hydrocarbon that constitutes the principal part of natural gas. The equations for the reactions involved are as follows:



The resulting carbon dioxide and hydrogen are separated as in the Bosch process. In a similar way, hydrogen may be obtained from other hydrocarbons (compounds made up of hydrogen and carbon).

Some hydrogen is also prepared by the electrolysis of water and by the action of steam on iron. Hydrogen is set free in the manufacture of certain important substances such as chlorine (which see) and the alcohol known as butanol. This is known as *by-product hydrogen* and is utilized whenever possible. For many purposes, especially where complete freedom from air and moisture is desired, hydrogen may be obtained in a 3 : 1 mixture with nitrogen by the catalytic decomposition of ammonia. The use of hydrogen in this manner greatly reduces transportation costs because 100 lb of liquid ammonia may be shipped in a container weighing no more than the heavy cylinder required for 200 cu ft of hydrogen, and yet the 100 lb of ammonia may be decomposed to give about 3300 cu ft of hydrogen at the point where it is to be used.

Properties. Hydrogen, like oxygen, is a colorless, odorless, and tasteless gas. The solubility of hydrogen in water is very small, only about one half that of oxygen. One liter of it weighs 0.08987 g, which indicates that the gram-molecular weight is approximately 2.013 ($22.4 \times 0.08987 = 2.013$). Thus the hydrogen molecule, like the oxygen molecule, contains 2 atoms ($\frac{2.013}{1.008}$). Hydrogen is the lightest of all known substances, being 14.385 times as light as air; it may therefore be transferred from one vessel to another by pouring it upward (Fig. 68).

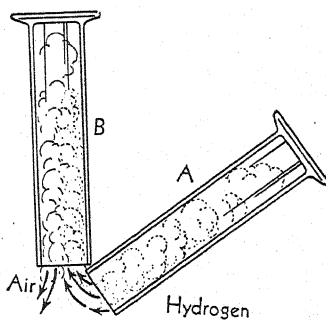


FIG. 68. The Hydrogen from Cylinder A Rises to the Top of Cylinder B and Displaces the Air

Velocity of hydrogen and other molecules. We know that the velocity which gas molecules have is inversely proportional to the square root of their molecular weight (Graham's law, p. 72). Light molecules move faster than heavy ones. The table below gives the average velocities of travel, in centimeters per second, at 0° C for the molecules of several of the gases present in the atmosphere.

GAS	MOLECULAR WEIGHT	AVERAGE MOLECULAR VELOCITY AT 0° C
Hydrogen (H ₂)	2.016	18.39×10^4 cm/sec
Helium (He)	4.003	13.11×10^4 cm/sec
Water (H ₂ O)	18.016	7.08×10^4 cm/sec
Neon (Ne)	20.183	5.61×10^4 cm/sec
Nitrogen (N ₂)	28.016	4.93×10^4 cm/sec
Oxygen (O ₂)	32.000	4.61×10^4 cm/sec
Argon (A)	39.944	4.13×10^4 cm/sec
Carbon dioxide (CO ₂)	44.01	3.92×10^4 cm/sec

A velocity of 1 mile/sec is about 16.1×10^4 cm/sec. Hence, of the gas molecules listed, hydrogen travels a little faster than 1 mile/sec, and carbon dioxide only about $\frac{1}{4}$ mile/sec. The projectile from the longest-range guns travels about 17×10^4 cm/sec.

Escape of hydrogen from atmosphere. The question of why such a relatively small quantity of hydrogen is present in the earth's atmosphere is an interesting one, since it is likely that at one time the quantity was large, and it is likely that hydrogen is still being formed and liberated into the atmosphere. While the average velocity of hydrogen molecules is only a little greater than 1 mile/sec, some of the molecules acquire energy at the expense of other molecules with which they collide and achieve velocities much in excess of the average. Such a fast-moving molecule, high in the atmosphere, could actually escape from the earth. Thus, gradually, over long periods of time, hydrogen has been dissipated from the atmosphere into outer space. The "escape velocity" is 1.1×10^6 cm/sec, or about 7 miles/sec, for any body moving away from the earth.

The moon has no atmosphere at all, because the moon's gravitational attraction is so small that molecules even of the heavier gases may there attain the "escape velocity" of 2.4×10^5 cm/sec, or about 1.5 miles/sec.

Liquefaction of hydrogen. The English investigator Dewar was the first to obtain hydrogen in the liquid state. He cooled the gas to a very low temperature by means of liquid air, and at the same time subjected it to a pressure of 180 atm. In this way it was obtained as a colorless, transparent liquid, boiling at -252.7° under a pressure of 1 atm. This is the lightest liquid known, having a

density of but 0.07 at its boiling point. When liquid hydrogen is evaporated under very small pressure, solid hydrogen is obtained as a transparent, snowlike body melting at -259.1° .

Occlusion of hydrogen. A large number of metals have the property of absorbing, or *occluding*, hydrogen. The quantity so absorbed by most of the metals is not large, but a few, especially platinum and palladium, take up large volumes of the gas. The quantity absorbed varies not only with the metal but also with the physical condition of the metal, as well as with the temperature and pressure under which the absorption takes place. One volume of palladium, in the form of a powder, at ordinary temperatures absorbs over 800 volumes of the gas. It is because of this property that hydrogen, when conducted into hot tubes made of iron or platinum, passes through the walls of the tube to a considerable extent.

The absorption of hydrogen by palladium can be strikingly shown by using strips of this metal as electrodes in the decomposition of water by the electric current. When the circuit is closed, oxygen is at once evolved at one electrode and hydrogen at the other. It will be noted, however, that the amount of hydrogen evolved as bubbles is relatively small at first, but gradually increases as the palladium becomes saturated with the gas.

Chemical conduct. Although hydrogen is inactive at ordinary temperatures, nevertheless under proper conditions it combines directly with many of the elements and even decomposes some compounds by uniting with elements present in them. Just as the compounds of oxygen with any other one element are called *oxides*, so those containing hydrogen in combination with another element are, as a class, known as *hydrides*, though this name is usually restricted to compounds of hydrogen with metals. Many of the non-metallic hydrides have other names.

1. **Action of hydrogen upon elements.** At suitable temperatures hydrogen combines directly with sodium to form the solid sodium hydride (NaH); with nitrogen to form the gaseous compound known as *ammonia* (NH_3); with sulfur to form the gas known as *hydrogen sulfide* (H_2S); and with chlorine to form *hydrogen chloride* (HCl). Although a mixture of hydrogen and chlorine does not react in the dark at room temperature, it explodes with great violence when exposed to direct sunlight.

Hydrogen is especially characterized by its affinity for oxygen, with which it combines to form water. *Experiments show that the ratio in which these two gases combine is 1 of hydrogen to 7.94 of oxygen by weight, or 2 of hydrogen to 1 of oxygen by volume.* A large

amount of heat is set free in this reaction. If we start with hydrogen and oxygen, at 18° and under a pressure of 1 atm, then for each gram of hydrogen entering into combination with the oxygen there is liberated 28,680 cal if the water produced remains in a state of vapor, or 33,920 cal if the resulting vapor is condensed to liquid form.

The union of hydrogen and oxygen, and the resulting formation of water, is shown by burning hydrogen in oxygen or air.

The hydrogen is generated in flask *A* (Fig. 69) and passed through the tube *B* filled with porous calcium chloride, which removes the moisture from the gas. *After the air has been displaced from the apparatus*, the hydrogen escaping at the jet is ignited. Almost instantly a dewlike substance is deposited on the cold sides of the jar *C*. This may be collected and proved to be water.

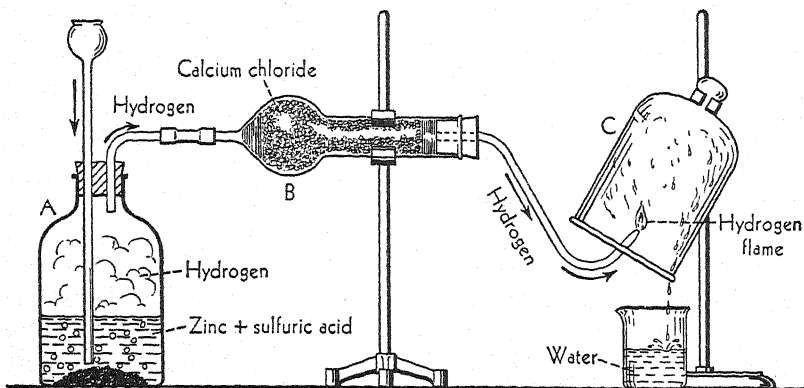


FIG. 69. Diagram of Apparatus Used for Burning Hydrogen in Air

The hydrogen, if pure, burns with a colorless but very hot flame. When burned in air much of the heat resulting from the union of the hydrogen and oxygen is absorbed in heating the inert nitrogen present. To obtain the maximum temperature one must use pure oxygen instead of air. Moreover, the hydrogen and oxygen must be brought together in the proportion in which they unite; otherwise the gas which is left uncombined will absorb a portion of the heat by being uselessly heated.

Explosion of a mixture of hydrogen and oxygen. While it is possible to burn hydrogen safely in air or pure oxygen by limiting the amounts of the two gases brought into contact with each other at any instant, mixtures of the gases in any considerable quantities explode with terrific violence when ignited. This situation presents a constant hazard when working with hydrogen.

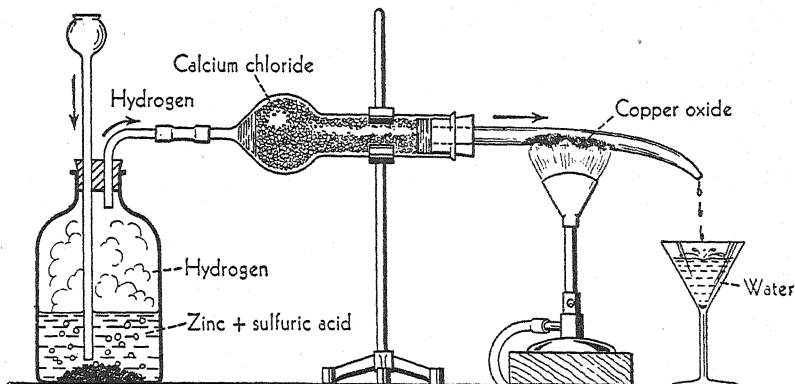
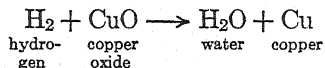


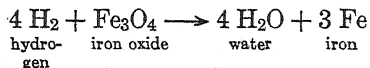
FIG. 70. Diagram of Apparatus Used for Reducing Copper Oxide with Hydrogen

2. Action of hydrogen upon compounds. Hydrogen not only combines directly with many elements, such as chlorine and oxygen, when present in the free state, but under favorable conditions it will remove these elements from some of their compounds.

Action of hydrogen on copper oxide. Hydrogen combines with the oxygen present in heated copper oxide (Fig. 70) to form water, which condenses in the colder portions of the tube near the end, while the black color of the oxide of copper gradually gives way to the reddish tint of copper as the action progresses. The change may be represented as follows:



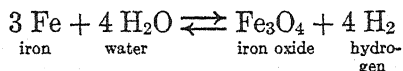
Many other metallic oxides, such as that of iron, may be substituted for the oxide of copper in this experiment. When oxide of iron is used, the change may be represented as follows:



Reduction; reducing agent. When oxygen is removed from a compound, the change is known as *reduction*. The compound from which the oxygen is removed is said to be *reduced*, while the substance which unites with the oxygen is called the *reducing agent*. Thus, in the experiment with the oxide of copper the hydrogen is called the reducing agent and the copper oxide is said to be reduced. It will be observed that reduction is just the reverse of oxidation. In the latter process oxygen is added to a substance, and in the former it

is taken away. More comprehensive definitions of the terms *oxidation* and *reduction* will be given in a later chapter.

The reaction between hydrogen and oxide of iron. It will be observed that the reaction which takes place when hydrogen is passed over heated iron oxide (see above) is just the reverse of that which takes place when steam is passed over red-hot iron (p. 103). In the one case hydrogen and iron oxide react to form water and iron; in the other the iron and water react to form iron oxide and hydrogen. The two reactions may be expressed as follows:



Whether the reaction goes in the one direction or the other or in both directions at the same time depends upon the conditions under which the reaction is carried out. The subject will be treated in detail in the chapter on equilibrium.

Physiological action of hydrogen. Pure hydrogen is not poisonous and may be breathed without danger, but the sulfuric acid and zinc used in its preparation frequently contain small amounts of arsenic, and the hydrogen generated from such substances is mixed with a gaseous compound of arsenic and hydrogen which is exceedingly poisonous and *must not* be inhaled.

Uses of hydrogen. Enormous quantities of hydrogen are required to meet its many commercial uses. Chief among these are the following: (1) in the manufacture of ammonia, which is used in many ways, especially for the production of fertilizers; (2) for the "hardening" of certain vegetable and animal oils, such as cottonseed oil, whereby these oils are converted into solid or semisolid fats suitable for use as food and in the manufacture of soap; (3) for the "hydrogenation" of coal, whereby the coal is partially converted into lubricating oils, gasoline, and other products; (4) in the manufacture of methyl alcohol (known also as methanol and wood alcohol); (5) to provide a reducing atmosphere for furnaces for annealing and deoxidizing brass; (6) for preventing the oxidation in an electric furnace of tungsten and molybdenum wire; (7) for cooling large electric generators and transformers; (8) for many laboratory purposes.

Hydrogen was formerly used (and is still, to a limited extent) for inflating balloons and airships. The fact that it is combustible makes it a dangerous gas to use for this purpose, so that in America it is being replaced by the noncombustible gas helium, as will be described in a later chapter.

Questions

1. Are any of the methods for preparing hydrogen similar in principle to any of those for preparing oxygen?
2. (a) What properties have oxygen and hydrogen in common? (b) In respect to what other properties do they differ?
3. Suppose you were to drop a piece of sodium into a beaker half filled with water, and some sodium peroxide into a second beaker of water. What products would be formed in each case?
4. What action will take place when iron (heated if necessary) is brought in contact with each of the following: (a) hydrochloric acid; (b) sulfuric acid; (c) steam; (d) oxygen; (e) hydrogen?
5. What products are formed when steam is passed over (a) hot iron; (b) hot carbon; (c) hot iron oxide?
6. Suppose you were to place some iron and water in a strong iron bomb and then heat the bomb. What substances would the bomb then contain?

Problems

1. Calculate the volume of 1 kg (a) of oxygen; (b) of hydrogen.
2. Suppose you wish to prepare 150 l of hydrogen by the action of sulfuric acid on zinc. What weight of sulfuric acid containing 25 per cent of hydrogen sulfate would be required?
3. Suppose you are asked to prepare as much hydrogen as possible from 500 g of water. Would you make use of (a) the electrolysis of water; (b) the action of sodium on water; (c) the action of hot iron on water; (d) the action of hot carbon on water?
4. Fifty liters of hydrogen and 40 l of oxygen were mixed together in a strong vessel and heated until combination took place. (a) What substances were then present in the vessel? (b) Calculate the weight of each substance.
5. Calculate the heat evolved by burning 200 l of hydrogen to form water vapor.
6. The atomic weight of the metal thorium is 232.12, and 29.01 g of this metal displaces 0.5016 g of hydrogen from hydrochloric acid. What is the valence of thorium?

Reading References

- LEONARD. *Crusaders of Chemistry*. Chapter VIII gives an interesting account of the life and discoveries of Cavendish.
- RIEDEL. *Industrial Chemistry*. Industrial methods for preparing hydrogen are discussed on pages 312-319.
- WEEKS. *The Discovery of the Elements*. Pages 29-33 tell of the discovery of hydrogen.

CHAPTER 8

The States of Matter and Their Transitions

Kinetic and van der Waals forces among particles. In any assembly of particles we can recognize two opposing tendencies. There is the tendency of the particles to fly apart because of their kinetic energy; and there is the tendency of the particles to be drawn together by attractive forces. These forces are enormously greater than the force of gravity, but are only effective over extremely small distances, comparable with the diameter of atoms. They are electrical in nature, but they are not to be confused with chemical bonds. They are usually called van der Waals forces. Their strength depends not only on the distance between molecules but also on the nature of the molecules.

If these forces are very large, as between particles of sugar, then the particles are likely to be bound together in a solid state, say at room temperature. With another kind of particle, such as hydrogen, the attractive forces at this temperature may be relatively so small that the tendency to fly apart predominates, and the particles exist as a gas. Forces of an intermediate magnitude may result in the formation of a liquid (as water) in which the molecules are bound close together *but are not rigidly bound*; they can glide freely over one another and so a liquid assumes no definite form.

LIQUIDS

Liquids and gases. Liquids, as we might therefore expect, differ from gases and do not distribute themselves uniformly throughout the whole volume of a containing vessel, but retain their own volumes. Because of their mobility, however, liquids do take the shape of the portion of the containing vessel which they occupy. Further, liquids contract only slightly even upon application of great pressure — a result which finds a ready interpretation in terms of our picture of the molecules of a liquid as being already crowded together with little free space between molecules.

Surface tension. A molecule A (Fig. 71) in the body of a liquid may be regarded as affected by all the molecules within a circum-

scribed sphere of very small radius, and the attraction in one direction is balanced by an equal attraction in the opposite direction.

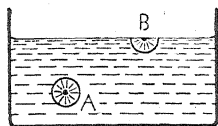


FIG. 71. Diagram Illustrating Surface Tension

This is not true of a molecule *B* in or near the surface of the liquid. All the particles within the indicated hemisphere pull it back toward the body of the liquid, and there is no opposing force to pull it upward. This inward pull tends to remove molecules from the surface, and to cause the surface to become smaller, just as though the surface were under a strain or tension. This

shrinking tension is called *surface tension*; and as a result of it small quantities of a liquid are drawn into spherical drops (Fig. 72)

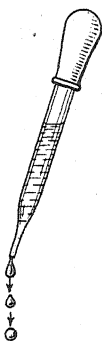


FIG. 72. Diagram Showing the Spherical Form of the Free Drops of a Liquid

because the area of a sphere is smaller than that of any other shape which a given volume of liquid can assume. Surface tension is a factor in the rise of liquids in capillary tubes and their penetration into the very small channels and crevices of porous materials.

Viscosity of liquids. All liquids flow, but there is always some resistance, within the liquid itself, to flow. This internal resistance to flow is called *viscosity*. Viscosity is often measured by the rate at which a liquid flows, under a given pushing force, through a long capillary tube (Fig. 73). Liquids like ether and alcohol, and even water, flow relatively easily and are said to be *slightly viscous* and are

also sometimes called *mobile*. Lubricating oil and molasses, on the other hand, are *highly viscous*. The viscosity of a liquid depends to a great extent on the magnitude of the van der Waals forces of attraction between the molecules. If these forces are large, the molecules are likely to encounter great resistance to gliding and rolling over one another, and the viscosity will be high.

Viscosity, like surface tension, is important in many processes. The rate at which finely divided materials settle in a liquid medium depends to a considerable extent on the viscosity of the medium. The smaller the viscosity, the more rapid is the settling. The choice of a lubricating oil depends in large part on its viscosity.

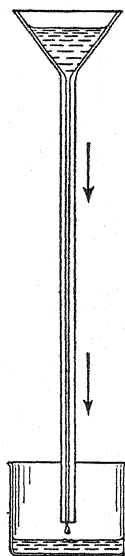


FIG. 73. Method of Measuring the Viscosity of a Liquid

TRANSITION BETWEEN LIQUIDS AND GASES

Evaporation. When a liquid such as water is placed in an open vessel, it gradually passes into the air in the form of gas or vapor, and the process is called *evaporation*. In a confined space, as in a closed bottle (Fig. 74), evaporation proceeds until the air above the liquid contains a definite percentage of gaseous water, and then apparently ceases; the air is said to be *saturated* with water vapor. It is only *apparently* that the process ceases, as we can understand if we consider the question from a kinetic point of view. The molecules of a liquid are in random heat-motion, some of them at speeds greater than the average and others at speeds less than the average. From the surface of the liquid the more rapidly moving molecules will from time to time escape, breaking free from the attraction of their neighbor molecules. They will then move about in the air space above as gas molecules, and will from time

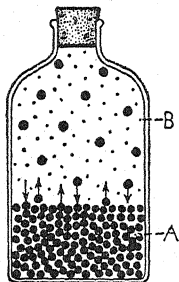


FIG. 74. Diagram of a Liquid (Large Black Dots) Evaporating into air (Small Dots) in a Closed Bottle

to time return to the liquid, as represented in Fig. 74. When the rate at which they return is equal to the rate at which they escape, a state of balance, or equilibrium, will be reached; and although molecules continue to escape, there is no further *net* loss of molecules from the surface. The air above the liquid is now said to be *saturated* with the vapor.

That it is the more rapidly moving molecules which escape during the evaporation of a liquid is evidenced by the fact that a liquid is cooled by the process of spontaneous evaporation, that is, by the escape of the more active ("hot") molecules.

NOTE. The term *equilibrium* is important and will be encountered frequently. It is used to designate the equality (balance) of two opposing tendencies or forces.

The effect of temperature upon evaporation. To heat a substance to a higher temperature is to increase the average speed of its molecules. So if a liquid A (Fig. 74) suffers a rise in temperature, more of its molecules break free from its surface, and the rate of evaporation is increased. A new equilibrium is reached at the higher temperature. The quantity of vapor over a liquid in a given closed space B (Fig. 75) increases rapidly with the temperature.

Vapor pressure. The quantity of vapor in equilibrium with a liquid at a given temperature may be expressed in a number of

ways. It might be stated simply as the weight in grams of the vapor in a liter of the space above the liquid. A more satisfactory way is to express it in terms of its *partial pressure* (p. 71), since the vapor, together with the gases composing the air, exerts a combined total pressure upon the surface of the liquid. *The vapor pressure of a liquid is the pressure upon its surface exerted by its own vapor when the liquid and the vapor are in equilibrium.* This pressure may be expressed in millimeters of mercury or in any convenient units of pressure. From another point of view, the vapor pressure of a liquid may be regarded as a measure of its tendency to evaporate. The variation of vapor pressure with temperature for a number of substances is shown in Fig. 76. A table showing the vapor pressure of water at various temperatures will be found in the Appendix.

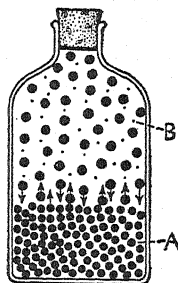


FIG. 75. Diagram of the Same Liquid as in Fig. 74, at a Higher Temperature

Example. The water vapor in air confined over water at 20° exerts a gas pressure equal to 17.53 mm. If the total pressure of the air is then 760 mm, 17.53 mm is due to water vapor and 742.47 mm to other gases. Therefore $\frac{17.53}{760}$ of the total volume of the air is water vapor. If the total volume is 1000 cc, then $\frac{17.53}{760} \times 1000 = 23$ cc is the volume the water vapor would itself occupy if it could be got as a gas at 760 mm pressure and at 20° .

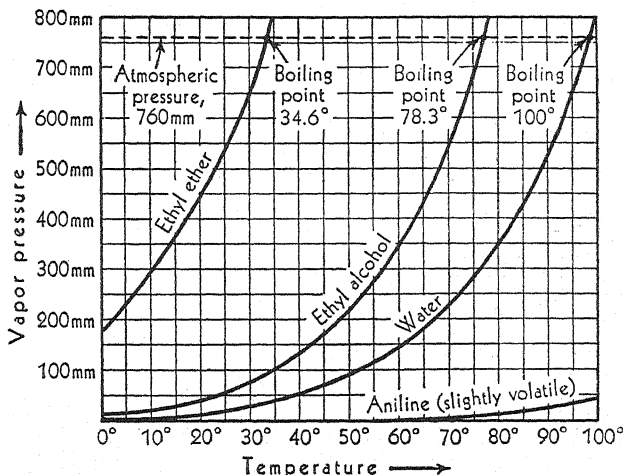


FIG. 76. Vapor-Pressure Curves, Showing Boiling Points of Several Liquids

Measurement of vapor pressure. Experimentally the value of the vapor pressure of a liquid at any temperature may be measured in many different ways. The instrument most commonly used, the manometer, is illustrated in Fig. 77. Another simple method is as follows: Two barometers,

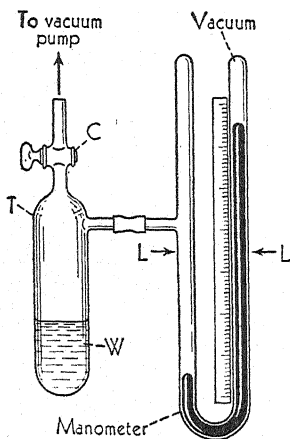


FIG. 77. Measurement of Vapor Pressure with a Manometer

A liquid, say water, *W*, is placed in the tube *T* and the stopcock *C* is opened to a vacuum pump. If air and water vapor are pumped out of the system on the left-hand side of the U tube, the two mercury levels will be *L, L*. Then if the stopcock is closed, the water evaporates and establishes an equilibrium vapor pressure at a given temperature. The difference in the level of the mercury columns indicates the vapor pressure of the liquid

measured in many different ways. The instrument most commonly used, the manometer, is illustrated in Fig. 77. Another simple method is as follows: Two barometers, with a Torricellian vacuum above the mercury column, are set up as shown in Fig. 78. A few drops of the liquid to be examined are introduced under the open end of *one* of the tubes. The liquid so introduced immediately rises to the top of the mercury column. Evaporation at once takes place, and, because of the pressure of the vapor so formed, the mercury column falls to some extent. When equilibrium is reached, the difference in level of the mercury in the two tubes (included between the dotted lines *A* and *B* in the figure) will measure the vapor pressure of the liquid in millimeters of mercury. The tube on the left is called the *control*. The tubes may be surrounded by jackets through which heated liquids are circulated, to secure any desired temperature.

Boiling point. During the heating of a liquid at

ordinary temperatures a portion of the energy given to it goes to raise its temperature, and a portion to change it into a vapor at its surface. When the pressure of the vapor arising from the liquid just exceeds the opposing atmospheric pressure, all the heat energy goes to change the liquid into vapor (in freeing the molecules from the attraction of their neighbors) and into mechanical work in pushing back the atmosphere. The temperature then remains constant, notwithstanding that heat is being applied to the liquid. This temperature is called

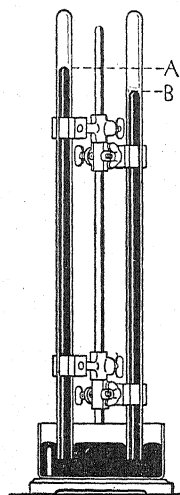


FIG. 78. Apparatus used in Determining Vapor Pressure

the boiling point under the pressure in question. *The boiling point may be defined as the temperature at which the vapor pressure of the liquid just exceeds the opposing pressure of the atmosphere.* The boiling point at standard atmospheric pressure is often called the *normal boiling point*. By suitably altering the pressure on a liquid, it may be caused to boil at temperatures higher or lower than its normal boiling point (Fig. 79).

Formation of bubbles. We usually think of a liquid as boiling when bubbles form and rise freely through it, and this is really an accurate test, as will be seen by reference to Fig. 80. The figure represents a vessel *A* in which water is being heated under an atmospheric pressure of 760 mm. When the whole body of water has been brought to a temperature of 100° , vapor escapes very rapidly from the surface. But the water in the interior or toward the bottom of the vessel, which is slightly superheated, does not wait until it comes to the surface but vaporizes where it is, and blows little bubbles with its vapor. In order that such a bubble *B* may form and survive, the pressure of the water vapor within the bubble must be a little greater than the hydrostatic pressure of the water lying above the bubble *plus the atmospheric pressure* transmitted by the water to the wall of the bubble. These bubbles, of course, rise to the surface as they are formed. Thus, the appearance of vapor bubbles (not to be confused with bubbles of dissolved air) in a heated liquid is a sure signal that the boiling point has been attained, that is, that the vapor pressure slightly exceeds the atmospheric pressure.

Volatility of liquids. Liquids differ greatly among themselves in the magnitude of their vapor pressures at a given temperature. At ordinary temperatures some of them, such as ether, alcohol, and benzene, have a high vapor pressure and consequently a low boiling point. Such liquids are said to be *volatile*. They evaporate very

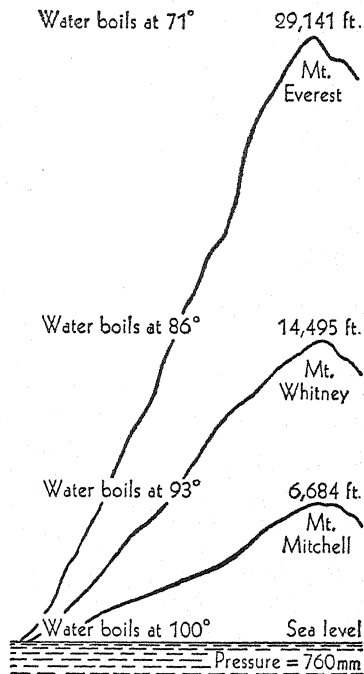


FIG. 79. Boiling Point of Water at Various Heights

rapidly when exposed to the open air. Other liquids, such as lubricating oils or mercury, have very low vapor pressures and correspondingly high boiling points.

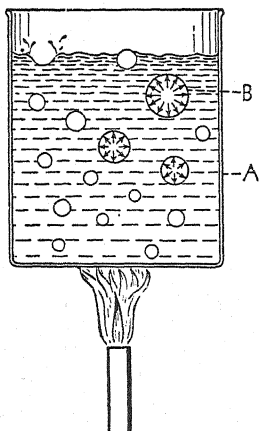


FIG. 80. *Diagram Illustrating the Behavior of Bubbles in a Boiling Liquid*

Heat of vaporization and condensation. Since only the fastest-moving ("hottest") molecules in a liquid are able to escape through its surface, the liquid becomes colder when it loses these molecules. Heat must be supplied to maintain the evaporation. The quantity of heat absorbed in changing 1 g of a liquid into 1 g of vapor at constant temperature is called the *heat of vaporization*. This is usually measured at the boiling point of the liquid. For water this is exceptionally large and amounts to 539 cal. Conversely, condensation of a gas or vapor to a liquid liberates a quantity of heat exactly equal to the heat of vaporization. This is called the *heat of condensation*.

Critical points. In the early days of experimentation with gases, there were no satisfactory methods for storing or transporting any considerable quantity of a gas, and investigators found it necessary to generate and purify the gases as they were needed for their researches. At the present time it is possible to purchase a large number of remarkably pure gases, such as nitrogen, oxygen, hydrogen, carbon dioxide, sulfur dioxide, and ammonia. These are supplied in highly compressed form in strong steel cylinders fitted with suitable valves and couplings. If we could equip tanks of these gases with small windows so that we could see the contents, we should learn a rather startling fact. The tanks of oxygen, nitrogen, and hydrogen contain nothing but highly compressed gas, while those of carbon dioxide, sulfur dioxide, and ammonia contain *liquid* as well as gas. How can we account for this difference in behavior in the two groups of gases?

To find an answer to this question let us approach the problem from a somewhat different angle. If a liquid is sealed within a tube A (Fig. 81) from which all air has been with-

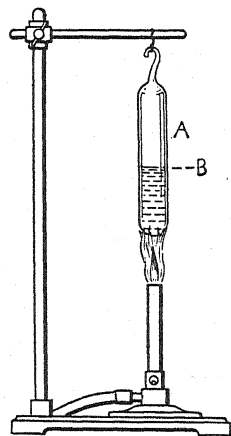


FIG. 81. *Drawing Illustrating the Critical Temperature of a Liquid*

drawn, the lower end of the tube will be filled with liquid and the upper end will contain vapor. If the liquid is now heated gently, more and more of it is vaporized, and the pressure in the confined space increases rapidly. The density of the remaining liquid diminishes, and the density of the vapor increases. At some temperature the two will become identical, and the boundary line between them, *B* (the *meniscus*), will fade out. The temperature at which this occurs is called the *critical temperature*, and the pressure exerted by the vapor at this temperature is the *critical pressure*. One may say that *the critical temperature is the temperature above which it is impossible to liquefy a gas, no matter how great a pressure be applied to it*. The critical pressure is that pressure which at the critical temperature just serves to liquefy the gas. The critical temperature and pressure of a few gases are given in the following table :

Table of Critical Temperatures and Pressures

GAS	MELTING POINT	BOILING POINT	CRITICAL TEMPERATURE	CRITICAL PRESSURE IN ATMOSPHERES
Hydrogen	- 259.1°	- 252.7°	- 239.9°	12.8
Nitrogen	- 209.8°	- 195.8°	- 147.1°	33.5
Oxygen	- 218.4°	- 183.0°	- 118.8°	49.7
Sulfur dioxide	- 75.5°	- 10.0°	157.2°	77.7
Ammonia	- 77.7°	- 33.3°	132.4°	111.5
Water	0.0°	100.0°	374.0°	217.7
Carbon dioxide	- 56.6°	(Sublimes at - 78.5°)	31.1°	73.0

Critical temperature and molecular behavior. We have previously seen that it is the attractive forces between molecules which bind them in the liquid state and produce such effects as surface tension. With rising temperature the average speed of the molecules in a liquid increases. If the speed becomes great enough (high temperature), there will come a point (critical temperature) where the attractive forces are entirely overcome by the increased speed, and there can be no liquid, even if the gas is compressed into a space no larger than a liquid would occupy. The surface tension of a liquid will therefore diminish with increased temperature and vanish entirely at the critical temperature.

Deviations from the gas laws. The gas laws which were described in the preceding chapter do not hold exactly true; they are really only *good approximations*. For example, Boyle's law and Charles's law hold quite well at ordinary temperatures and pressures; but if

the gas is highly compressed (or greatly cooled), we observe experimentally that the gas shrinks to a smaller volume than we should expect from the law. This is because the molecules have now been crowded together sufficiently in a relatively small volume to allow the van der Waals forces to operate. As a result the molecules are drawn even more closely together into a still smaller volume. Many modified gas-law equations have been proposed to correct for this effect.

The actual volume of the molecules themselves (in contrast with the volume through which they dart) also is responsible for deviations from perfect gas-law behavior. The gas laws would hold exactly only for a perfect gas, that is, a gas whose molecules are mere geometric points, which do not exert van der Waals forces. No such gas exists; it is purely imaginary.

Liquefaction of gases — historical. The earliest systematic efforts at liquefaction of gases were those of the English scientist Faraday (Fig. 184),

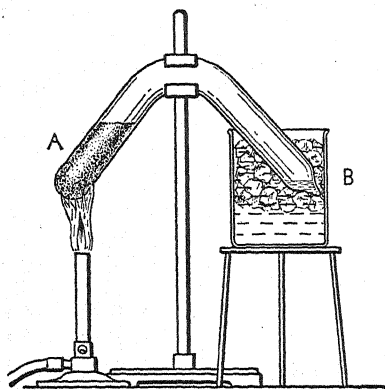
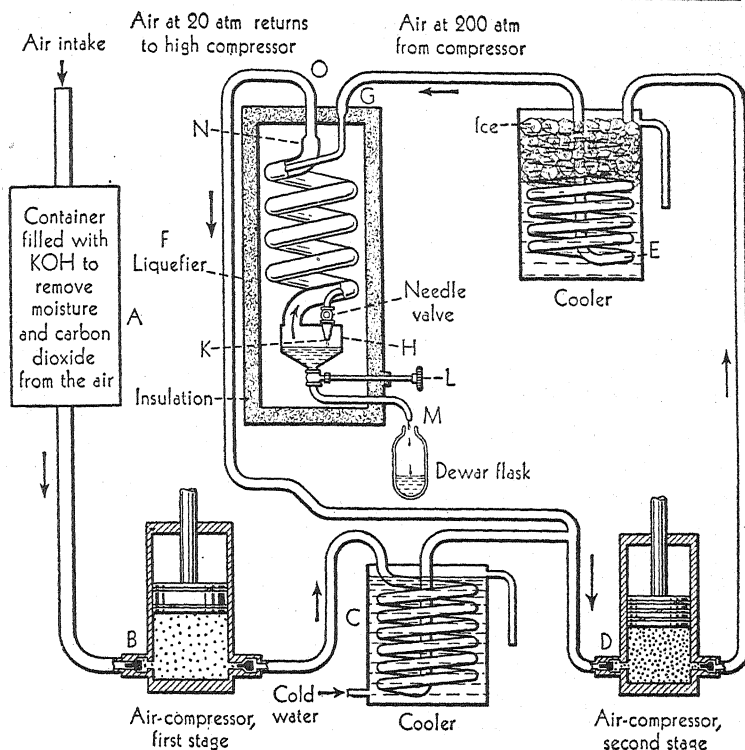


FIG. 82. Faraday's Method for Liquefying Gases

about 1823. He relied upon the effect of pressure, together with moderate cooling, and most of his experiments were carried out in the following way: A quantity of solid material which, when heated, would liberate a considerable quantity of the gas to be liquefied was placed in one end of a bent tube. The other end was sealed and the tube arranged as shown in Fig. 82. A is the solid material and B a cooling bath of ice water. When the solid is heated, the gas is given off in a confined space and, being under great pressure, liquefies in the cold portion of the tube. In this general way Faraday liquefied a number of gases, such

as chlorine, ammonia, and carbon dioxide. He was unable to liquefy other gases by this method and called these permanent gases.

Liquefaction of gases. If the critical temperature of a gas is somewhat above ordinary temperatures, the gas can be liquefied by pressure alone. For example, at 20° carbon dioxide (critical temperature 31.1°) is liquefied by a pressure of 56.3 atm. With gases of low critical temperatures the difficulty lies in securing the low temperature, since the requisite pressure is readily available. In modern practice *the gas is made to cool itself* by purely mechanical methods. One of the procedures is based on the following principle: Most compressed

FIG. 83. *The Steps in the Liquefaction of Air*

The air enters the apparatus at the air intake and passes through the chamber A, filled with absorbents for moisture and carbon dioxide. It then enters the air-compressor B, where it is highly compressed. Heat is evolved in this process, and the compressed hot air is cooled by cold water in the cooler C. It undergoes further compression in D and is again cooled in E. The highly compressed cold air then enters the liquefier F. Inside the liquefier the copper tube G is enclosed in a tube N of larger diameter, and the two concentric tubes form a spiral. At K there is a very small opening controlled by a needle valve. Through this hole some of the compressed air escapes into the cup H and expands to a lower pressure. In expanding, the air becomes very cold, and is led back through the outer tube N to cool the incoming air within the inner tube G. As the process continues, the air in tube G becomes increasingly cold until it reaches the temperature of liquefaction, when drops of liquid air form and collect in the cup M. By means of the valve L, the liquid air is drawn off into the Dewar flask through M. The cold expanded air returns to the compressor D through the pipe O.

gases become cooled when *throttled* to a lower pressure, that is, when allowed to escape through a small opening or a nozzle from a higher to a lower pressure. This cooling is known as the Joule-Thomson effect, and is to be explained in terms of the attractive forces between the gas molecules. When the molecules of the compressed

gas move apart into a larger volume at the lower pressure, they separate from one another against the attractive forces holding them together. To accomplish this work of separation requires energy. This energy is taken from the heat energy of the gas itself; consequently the gas is cooled. If now this cold gas is allowed to flow back over the compression vessel, the compressed gas may become so cold that, after the still further cooling produced by the throttling, it will liquefy. The details of the liquefaction of air by this method are shown in Fig. 83.

Dewar flasks. For collecting and temporarily preserving such liquids as liquid air, whose boiling point is far below the temperature of an ordinary room, it is essential that the container be well insulated. Dewar flasks (Fig. 17, p. 22) are employed for this purpose. Liquid air may be preserved in such a vessel for many hours. Thermos bottles of the same plan of construction are now familiar utensils for keeping liquids either hot or cold during long journeys, and are very effective.

Mechanical refrigeration; ice machines. Mechanical refrigerators (Fig. 84) and ice-making machines all utilize the cooling effect of

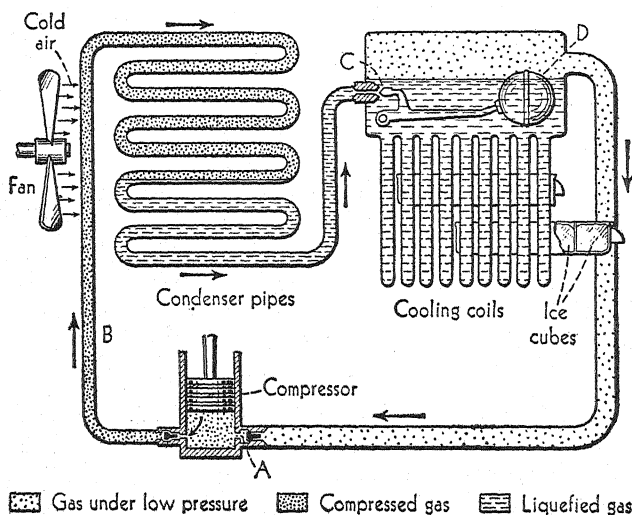


FIG. 84. Diagram to Show How the Electric Household Refrigerator Operates

The gas used enters the compressor at A. The compressed gas is forced upward through the pipe B, is cooled by the fan, and liquefies in the condenser pipes. The liquid then enters the icebox at C, where it evaporates, cooling the liquid in the coils to a low temperature. The evaporated gas returns to the compressor. The float-valve D gradually falls as the liquid evaporates, thus allowing more of the liquid to enter the icebox at C. The valve rises with the surface of the liquid, being adjusted so as to close again the pipe at C when the desired volume of the liquid has been admitted.

expanding gases and the absorption of heat by the vaporization of low-boiling liquids. The two important economic factors are (1) the relative ease of compression to the liquid state and (2) the magnitude of the heat of vaporization. In small domestic refrigerators, sulfur dioxide, formerly used almost entirely, is now being replaced to a considerable extent by dichlorodifluoromethane, CCl_2F_2 , and related compounds, which are odorless and nontoxic. For cold-storage rooms and ice machines ammonia is largely used.

The following table gives the significant constants for some of the gases that have been or are being used in refrigeration :

Gas	CRITICAL TEMPER- ATURE	CRITICAL PRESSURE	BOILING POINT	HEAT OF VAPORIZATION (Calories per Gram)		
				-10°	0°	10°
Ammonia (NH_3)	132.4°	111.5	- 33.3	309.9	301.8	293.1
Carbon dioxide (CO_2)	31.1°	73	—	62.67	56.15	48.5
Sulfur dioxide (SO_2)	157.2°	77.7	- 10.0	—	91.2	88.7
Methyl chloride (CH_3Cl)	143°	66	- 23.7°	98.5	96.9	95.1
Ethyl chloride ($\text{C}_2\text{H}_5\text{Cl}$)	187.2°	52	12.2°	95.5	93.9	92.0
Dichlorodifluoromethane (CCl_2F_2)	111.5°	39.56	- 29.8	38.6 (- 15°)	—	33.1 (30°)

TRANSITION BETWEEN SOLIDS AND LIQUIDS OR GASES

Solid substances. When a liquid substance is cooled, it becomes less and less fluid. At a sufficiently low temperature all liquids become rigid, and we call this form a *solid*. As a rule, the change from liquid to solid is sudden. At some definite temperature small crystals begin to form, and the temperature of the liquid comes to a *perfectly definite value* called the *freezing point*; and this remains unchanged until all the liquid has solidified. For example, water solidifies, or freezes, at 0°. Solids formed in this way are always *crystalline*; and this indicates an orderly arrangement of particles within the solid. Occasionally there is no definite point of solidification, and the changes from the liquid state into that of a rigid substance are gradual. Glasses, glazes, glue, tar, and gums are examples of such materials. These are sometimes called *amorphous solids*, to distinguish them from crystalline solids; but it is better to consider them as still liquid but so viscous that they are almost as rigid as crystalline solids.

Freezing point. When a crystallizable liquid, such as water, is cooled, it does not always *begin* to crystallize at its freezing point. Indeed, liquid water has been cooled far below 0° without freezing. A liquid below its freezing point is said to be *undercooled*. If a crystal of the substance once forms, or if a "seed crystal" is dropped into the undercooled liquid, solidification at once begins, heat is given out in the process, and the temperature rises to the true freezing point and remains there as long as both liquid and solid are present. *The freezing point is defined as the temperature at which both solid and liquid will remain in contact with each other without change of temperature.* The more viscous a liquid is at its freezing point, the more readily undercooling takes place; and with very viscous liquids, as we have seen, true solidification may never occur.

Melting point. Conversely, when a crystalline solid is slowly heated, its temperature steadily rises to a certain definite point (unless the solid should undergo decomposition). Further application of heat does not raise the temperature, but the solid begins to melt. The temperature remains constant until the melting is complete, and then rises again. The heat energy supplied to the substance during the process of melting has no effect on the temperature, but is used up in altering the physical state of the substance. Obviously the temperature of the melting point and that of the freezing point are identical.

Heat of fusion and of solidification. The quantity of heat absorbed in converting 1 g of a solid at its melting point into 1 g of liquid at the same temperature is called the *heat of fusion* of the substance. For ice this amounts to about 80 cal. The heat given out when 1 g of a liquid at its freezing point solidifies to 1 g of solid is called the *heat of solidification*. The heat of solidification is the same in quantity as the heat of fusion, and represents the difference in energy between the orderly, rigid arrangement of molecules in a solid and the relative disorder and mobility of molecules in a liquid.

The rather large heat of fusion of water is of great importance in nature. If ice required little heat for melting, we should have disastrous floods on warm winter days. If water gave out little heat on freezing, all bodies of water save very large ones would freeze solid in severe winter weather.

Vapor pressure of solids. Many solids give off vapor at ordinary temperatures, just as do liquids. This is evident from the odor of such solids as camphor and naphthalene (moth balls). As the solid is heated, this vapor pressure increases. If it increases to the point where it just exceeds the pressure of the atmosphere, the solid cannot

be heated to a higher temperature in an open vessel, just as a liquid cannot be heated above its boiling point. To melt such a solid it is necessary to heat it in a closed vessel. This behavior is illustrated by solid carbon dioxide, whose vapor pressure reaches 760 mm at -78.5° , but which does not melt until -56.6° . At this latter point its vapor pressure is more than 5 atm. When the vapors from such solids are cooled, they pass directly back into the solid form. The

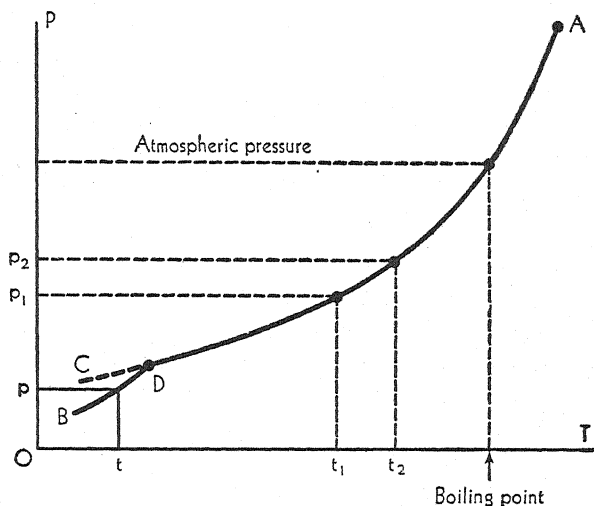


FIG. 85. Diagram Illustrating the Equilibria of the Three States of Matter

process of converting a solid into a vapor and cooling the vapor to a solid again is called *sublimation*, and the solid is said to *sublime* on heating. The corresponding process with liquids is called *distillation*. Solids which have a sufficient vapor pressure are often separated from nonvolatile impurities by sublimation, and this practice is the origin of such names as *corrosive sublimate* (mercuric chloride).

Equilibrium diagram. In the preceding pages we have seen that a number of different types of equilibrium exist in a system containing a substance in different physical states. Thus, with water we have an equilibrium between the vapor and the liquid; between the vapor and the solid; between the liquid and the solid. At every different temperature there is a different pressure exerted by the vapor on (1) the liquid or (2) the solid. We can show the general character of these two equilibria in a very compact form in a diagram (Fig. 85) in which we represent temperature by distances along the line OT and pressure by distances along the line OP . The curve DA is a plot of the experimentally measured vapor pressures of the liquid over

a range of temperatures — for example, the vapor pressure p_1 at temperature t_1 , and p_2 at t_2 . This curve ends at a point A , which is the critical temperature, above which the substance can no longer exist in the liquid state. DB is the vapor-pressure curve of the solid, usually called the sublimation curve. The point D , where these two curves intersect, is the freezing point of the liquid; and at that point the vapor pressures of solid and liquid are equal. Since the two curves intersect at this point, the solid, liquid, and vapor can coexist at this temperature and pressure; but they can do so at no other point. If no solid makes its appearance at the freezing point, the vapor pressure of the liquid will be represented by the extension of the curve AD toward C . It will be seen that the vapor pressure of such an undercooled liquid is greater than that of the solid at the same temperature, as at t . This indicates that the undercooled liquid is in a more unstable condition. Very few (if any) solids can be heated above the melting point without melting; so the curve BD can rarely be prolonged beyond the transition point.

Crystals. When a liquid freezes, it changes into a mass of solid bodies, which have a definite geometric form and are called crystals. Similar bodies may also be deposited from solutions or be formed by condensing vapors. A crystal is always bounded by plane surfaces, which are arranged in an orderly fashion with reference to imaginary lines drawn through the crystal and called its *axes*. Every crystal has therefore a definite geometric form. While the variety of form which crystals may assume is almost endless, it has been found that crystals may all be referred to one of *six fundamental arrangements* of axes, which are known as the six *crystallographic systems*. These arrangements, together with two of the simplest crystal forms in each system, are shown in the accompanying figures (Figs. 86–92).

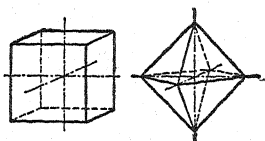
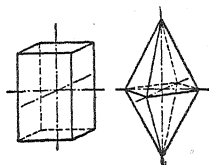
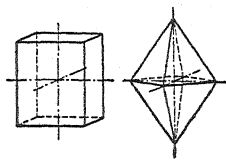
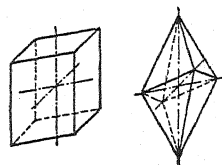


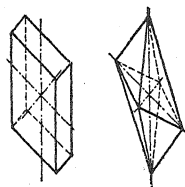
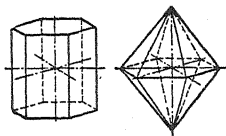
FIG. 86. *Isometric System*

The crystal systems. The relation of the axes in the several systems is as follows:

1. Isometric, or regular, system (Fig. 86): three equal axes, all at right angles to each other.
2. Tetragonal system (Fig. 87): two equal axes and a third of different length, all at right angles.
3. Orthorhombic system (Fig. 88): three unequal axes, all at right angles.
4. Monoclinic system (Fig. 89): two axes at right angles and a third at right angles to one of these but inclined toward the other. The axes may be of any relative lengths, and the angle of inclination may vary from 0° to 90° .
5. Triclinic system (Fig. 90): three axes, all inclined toward each other. The axes may be of any relative lengths, and the angles of inclination may also vary.

FIG. 87. *Tetragonal System*FIG. 88. *Orthorhombic System*FIG. 89. *Monoclinic System*

6. Hexagonal system (Fig. 91): three equal axes in the same plane, intersecting at angles of 60° , and a fourth at right angles to all of these. In addition to the two general forms shown in Fig. 91 there are many rhombic forms belonging to this system, such as the one represented in Fig. 92.

FIG. 90. *Triclinic System*FIG. 91. *Hexagonal System*FIG. 92. *Hexagonal System (Rhombic Form)*

Crystal form a characteristic of a substance. In general, under the same conditions, a given substance will always crystallize in a *form* which may be referred to the same system, with the same ratio of axis lengths and degree of inclination. The actual crystal *shape* may be quite different, however. For example, it may be either a cube or an octahedron, both of which are forms in the isometric system. Two different substances which crystallize in the same form or almost the same form are said to be *isomorphous*.

Allotropic forms. It is evident that the atoms composing an element or present in a compound might find it possible to arrange themselves in either of two (or more) patterns, just as we can pile oranges in two patterns by starting with a square base for one pile and a hexagonal base for the other. This would give rise to different crystalline forms with different physical properties and different chemical energies. This is actually observed to happen with a great many substances, both elements and compounds, and these modifications are called *allotropic forms*. For example, the diamond is carbon crystallized in the isometric system, while graphite is carbon crystallized in the hexagonal system.

A substance that crystallizes in two different systems is said to be *dimorphous*. For example, one form may occur when the substance freezes, and another when it is deposited from solution. *Trimorphous* substances are also known.

CRYSTAL STRUCTURE

The crystal lattice. Like gases and liquids, crystals are made up of particles of matter, namely, of atoms, molecules, or ions. The shape of a crystal is the consequence of the spatial arrangement of the particles within the body of the crystal. The very fact that every crystalline substance possesses a characteristic form must necessarily mean that its constituent particles always marshal themselves in space in a perfectly definite and always-repeated manner. Such an ordered array of particles in three-dimensional space is called a *crystal lattice*, or oftentimes a *space lattice*.

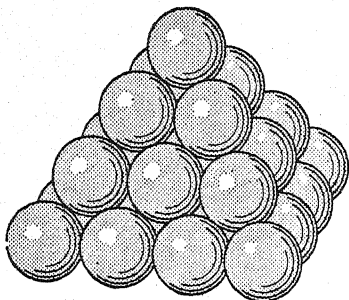


FIG. 93. A Crystal Lattice

A very familiar illustration of what is meant by a space lattice is shown in Fig. 93. This particular method of piling spheres together is employed by grocers in displaying their apples, oranges, and grapefruit; and one may often see cannon balls piled up in this fashion in old courthouse yards.

For about twenty-five years we have had available a very efficient method for finding the lattice structure of crystals. The method, which involves the use of X rays, was discovered by a brilliant German physicist, Laue. The details of the X-ray technique are complicated, and we cannot attempt to do more here than give a rough idea of the fundamental principles on which the method is based.

The X-ray method. The principle underlying this method may be explained very simply. Suppose we take a small block of mica, which, as everyone knows, has a laminated structure, and place it as in Fig. 94, so that a beam of monochromatic light (say from a sodium flame) falls upon the mica and is reflected into the eye. We see a series of alternate bright and dark lines on

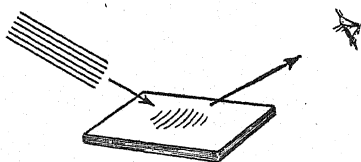


FIG. 94. Reflection of Light from Mica

the surface of the block. Some of the light is reflected from the *surface layer* of the mica, but some of the light penetrates *into* the mica and is reflected from successively deeper layers. As these various rays, reflected up from the different mica layers, join together again on the way to the eye, there are certain angles of reflection at which the rejoined light waves will all be in step (in phase), and reinforcement will occur, so that we see yellow lines. At any other angles the waves are out of step and blot one another out (interference), so that we see black lines.

Calculation of distance between mica layers. The mathematics that follows is very simple. Every college student knows that in a right-angled triangle, such as aOb (Fig. 95), the sine of an angle is the side opposite the angle divided by the hypotenuse; that is, $\sin \theta = ab/Ob$, or $\sin \theta = ab/d$. Therefore $ab = d \times \sin \theta$.

In Fig. 95, AB represents the surface layer of the mica, CD the next deeper layer, and so on. The approaching wave front of the light beam can be allowed to impinge on the mica at any angle that we please. If we suppose that the upper part of the beam, W , is reflected from AB , and the lower part of the beam, W' , is reflected from CD , it will be observed that W' has to travel a greater distance than W in reaching the eye.

If the angle θ is adjusted so that this extra length of path for W' (namely, the distance $ab + bc$) is exactly one whole wave length (or two or three or more whole wave lengths), then when W' rejoins W they will both be exactly in step again; but at angles slightly different from this particular value of θ , they will be out of step and they will interfere.

Now the angle aOb is also equal to θ , and ab is equal to $d \times \sin \theta$, where d is the distance between the two layers AB and CD . Then $ab + bc = 2d \times \sin \theta$. Therefore if $2d \times \sin \theta = \lambda$, where λ is a whole wave length, or if $2d \times \sin \theta = n\lambda$, where $n = 1, 2, 3, 4$, etc., reinforcement will occur. This equation, $2d \times \sin \theta = n\lambda$, provides a method for determining the distance between the mica layers; for if we know λ , the wave length, and if we measure the angle θ , we can calculate d . The only restriction is the provision that the wave length of the light employed must be of the same order of magnitude as the distance d between the layers.

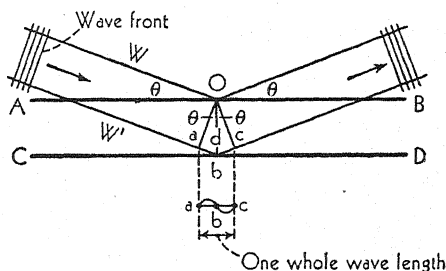


FIG. 95. Reflection from a Pile of Parallel Planes

X rays and the crystal lattice. Now in a crystal lattice there are many sets of parallel planes that can be drawn through the *particles*

— for example through the *atoms* out of which the lattice is built up. Naturally, then, these planes are populated with atoms. Exactly the same procedure may be employed to determine the distance between these atom planes as is used in the case of the mica layers, except that we must work with light of much shorter wave length (X rays), because the distance between the planes of a crystal lattice is much shorter than that between the mica layers. The manner in which X rays are generated will be described in a later chapter. Since the X-ray wave length is too short to affect the retina of the eye, we substitute a photographic plate or film for the eye. Knowing the wave length of the X ray employed, we can measure (by examination of the photographic film) the angle (θ) at which reinforcement in the reflected beam occurs, and then we can calculate the distance (d) between the layers of the atoms.

Working out a space lattice. Let us, then, allow a beam of X rays to fall at an angle θ on a face of a cubical crystal of sodium chloride, and determine the interlayer distance of the set of layers parallel

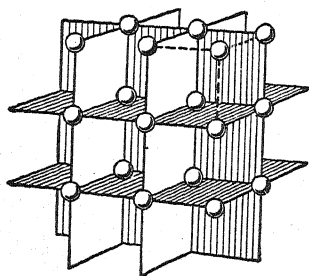


FIG. 96. *Mutually Perpendicular Intersecting Planes*

with this face. We then turn the crystal through an angle of 90° and determine the interlayer distance for planes perpendicular to the first set, and finally we go through the same procedure for the other set of layers perpendicular to the first two. In this way we determine the spacing of three sets of planes, all at right angles to one another, as shown in Fig. 96. Since all these planes are populated with atoms it follows that the points at which the three mutually perpendicular planes intersect will be occupied by atoms. Consequently we are able to mark out, by this method, the location of the atoms and hence determine the structure of the lattice.

The Laue method. In the original Laue method a pencil-like beam of X rays enters the crystal perpendicular to a face, passes directly through, and is caught on a photographic plate on the other side of the crystal. Many sets of lattice planes at various angles to the central X-ray beam (on its way through the crystal), and cutting across the path of the beam, co-operate with one another to reflect the X rays and to produce a pattern of reinforcement spots on the photographic plate. Over all the rest of the photograph interference blots out the X rays. Fig. 97 shows a Laue photograph of magnesium oxide. From the position of these spots and their size one can calculate the position of the intersecting lattice planes, and work out the position of the atoms in the lattice.

Results of X-ray analysis. The lattice structures of a great many crystals have been solved by means of X-ray analysis, and we may now glance at a few of the very simple ones. Others will be presented in connection with the appropriate compounds or elements.

Sodium chloride. Fig. 98 shows the crystal lattice of sodium chloride. The lattice is made up not of *molecules of sodium chloride* nor of *atoms of sodium* and *atoms of chlorine*, but of *sodium ions* and *chlorine ions*, that is, electrically charged atoms. In the lattice every sodium ion is surrounded by six chlorine ions: one above, one below, one in front, one behind, one to the left, one to the right. Likewise every chlorine ion is surrounded by six sodium ions. The conclusion that this lattice is made up of ions rather than of atoms also comes out

of the X-ray analysis, although we cannot follow through the argument here. This conclusion is of enormous importance to chemistry, as we shall see later on.

Fig. 98 gives only the position of the centers (nuclei) of the sodium and chlorine ions. These ions are not as small, nor are they separated from one another as far, as one might conclude from Fig. 98. The ions are probably actually "touching" one another, and Fig. 99 portrays the situation more satisfactorily and also indicates the relative sizes of the two ions.

Copper, silver, gold. The crystal lattices of metallic elements such as copper, silver, and gold are made up of *atoms*, not *ions*. Their atoms are arranged in the lattice as shown in Fig. 100. The only difference is that the three metals have atoms of different sizes. This type of lattice structure is called the *face-centered cubic*. Inspection of Fig. 100 will show that the lattice may be divided into little cubes. There is an atom in the center of every face of these cubes (as well as an atom at every one of the four corners of the face); hence the name. As a matter of fact, the face-centered cubic lattice is exactly the same as that of Fig. 93 (the groceryman's method of piling up spheres), although there the pile is viewed from a position different from that in Fig. 100. Most of the metals which are markedly plastic (that is, malleable and ductile) have their

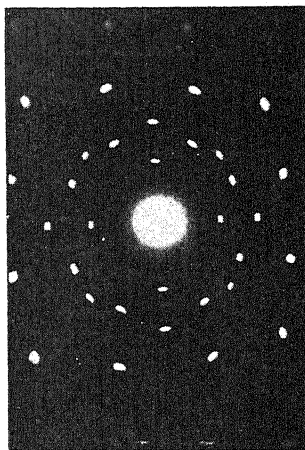


FIG. 97. *Laue Photograph of Magnesium Oxide*

atoms piled together in this face-centered cubic lattice, including (in addition to copper, silver, and gold) the metals calcium, aluminum, lead, nickel, platinum, and others. The nonplastic (hard or brittle) metals, such as vanadium, tantalum, chromium, molybdenum, tungsten, beryllium, magnesium, titanium, cadmium, zinc, and so on, crystallize in other types of lattices.

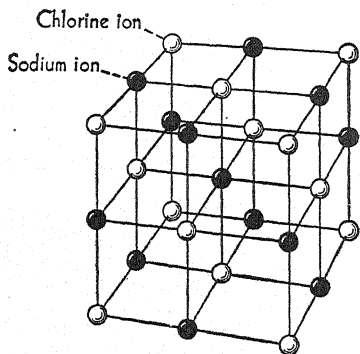


FIG. 98. *Diagram of the Crystal Lattice of Sodium Chloride*

that plane-slippage is relatively easy; whereas in some of the other types of lattices any slippage, if it occurs at all, is likely to end in a parting of neighbor planes, in faulting and fracture.

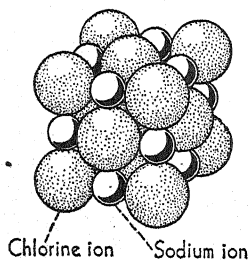


FIG. 99. *Crystal Lattice of Sodium Chloride*

The scope of X-ray analysis. It will be seen that X-ray analysis gives us a wonderful insight into the fundamental make-up of solid matter. This in turn throws much light upon the properties of matter *in bulk*, such as malleability, ductility, electrical conductivity, hardness, magnetic effects, solubility, melting point, allotropic changes, and many others. It enables us to investigate the way in which many materials of everyday life are put together, and aids us in understanding the properties of such things as natural minerals, alloys, the silicates, rubber, cellulose, muscle tissue, hair, bone, teeth, and hundreds of other materials.

The property of plasticity depends on the ease with which the planes of atoms within the lattice can slip past, or glide over, one another when an external deforming force is at work. The very geometry of the face-centered cubic piling is of such a sort

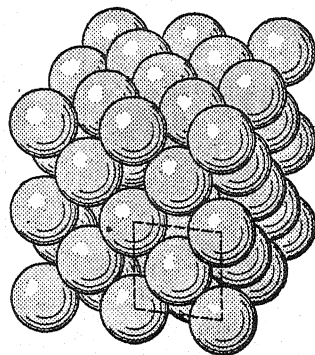


FIG. 100. *Face-Centered Cubic Lattice*

Questions

1. What are the characteristics of molecules which cause deviations from the gas laws? Under what conditions of temperature and pressure do these deviations become most pronounced?
2. In what way does the water content of the human body act to regulate the body temperature?
3. Why are liquids of high viscosity more likely to exhibit undercooling than liquids of low viscosity?
4. Why is water ideally adapted for use in hot-water heating systems?
5. In what way does the passage of a current of air over a liquid hasten evaporation?
6. (a) In general, should you expect liquids of high boiling point to have high or low vapor pressures at room temperature? (b) Why? (c) Should you expect pure solids of high melting point to have high or low tensile strength and high or low hardness? (d) Why?
7. When a liquid has been heated to its boiling point, heat must be applied to continue the boiling. Why?
8. (a) Can any of the compounds used in mechanical refrigeration (p. 125) be condensed to a liquid at ordinary temperatures? (b) Suppose you had 1 g of each of these in the liquid state; which would absorb the most heat in vaporizing?
9. (a) Would it be unreasonable to expect that a substance with a vapor pressure equal to or greater than 760 mm could exist below its melting point? (b) Would such a substance melt under ordinary conditions? (c) If not, could such a substance be obtained in liquid state?
10. Why is a region near a large body of water less likely to suffer a rapid change in temperature than one located elsewhere?

Problems

1. What is the weight of the water present in a liter of air saturated with water vapor at 30°?
2. How many calories of heat would be absorbed in the melting of 1 lb of ice at 0° to water at 0°?
3. How many calories of heat would be absorbed in transforming 1 g of ice at 0° into 1 g of water vapor at 100° (assume that the specific heat of water is 1.0 over the range 0° — 100°)?
4. A Dewar flask contains 1000 g of water. The temperature of the water is 25°. To this is added 100 g of ice of which the temperature is 0°. The flask is set aside until the temperature of the contents is constant. Calculate this temperature.
5. How many water molecules are there in 1 cc of Liquid water at 4°?

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- BRAGG. *Concerning the Nature of Things*. Chapter III tells of the nature of liquids. Chapters IV, V, and VI tell of the nature of crystals.
- CADY. "Liquid Air," *Journal of Chemical Education*, Vol. VIII, pp. 1027-1043. An excellent article with many illustrations.
- FARADAY. *The Liquefaction of Gases*, Alembic Club Reprints, No. 12. An account by Faraday of his experiments in liquefying gases.
- STILLWELL. "Chapters in Crystal Chemistry for College Freshmen," *Journal of Chemical Education*, Vol. X, pp. 590-599 and 667-674.
- "Symposium on Refrigeration and Refrigerants," *Industrial and Engineering Chemistry*, Vol. XXIV, pp. 601-630. An excellent discussion of the subject by a number of specialists in this field.
- The World Book Encyclopedia contains an excellent article about ice, with many illustrations.

CHAPTER 9

The Atmosphere: the Rare Gases; the Spectroscope; Nitrogen; Carbon Dioxide

Atmosphere and air. The term *atmosphere* is applied to the gaseous envelope surrounding the earth; the term *air* generally indicates a limited portion of this envelope, as the air in a room, although the two words are often used interchangeably. Despite the fact that air is invisible, we are often conscious of its presence—for instance, in our breathing. On windy days we feel it beating against our cheeks and blowing through our hair. Air, of course, like other matter, possesses inertia.

Weight of the atmosphere. We have seen already (Chapter 5) that the atmosphere is everywhere pressing down on the surface of the earth with a pressure equal to that exerted by a column of mercury 76 cm high, or with a weight of 1033 g/cm². This is equivalent to about 15 lb/sq in. (more nearly 14.7). Since this is the average weight of the atmosphere, at sea level, over every square inch of the earth's surface, we could easily calculate the total weight of the entire atmosphere if we knew the area in square inches of the earth's surface. The earth, approximately spherical in shape, has an equatorial diameter of 12,756 km, or about 7926 miles. The surface area of a sphere is πd^2 (d = diameter). Remembering, then, that there are 5280 ft in a mile and 12 in. in a foot, we find that the

weight of the atmosphere (in tons) = $\frac{14.7 \text{ lb}}{\text{sq in.}} \times \pi \times (7926 \times 5280 \times 12)^2$

sq in. $\div 2000 \text{ lb} = 5.82 \times 10^{15}$ tons, or 5820 million million tons! If proper allowance is made for the space occupied by land masses rising above sea level, a more accurate value of 5.70×10^{15} tons is obtained.

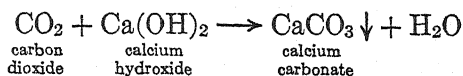
Height of atmosphere. It must not be supposed that the atmosphere is a layer of even thickness and of uniform density from bottom to top. As we climb a mountain or rise in an airplane, we find that the density and pressure decrease with increasing height. Finally, at great heights, the atmosphere fades out gradually into nearly empty space. At successive heights a given column of the

atmosphere supports a smaller and smaller amount of air lying above it. At about 3.6 miles (19,000 ft) the density and pressure are only one half what they are at sea level. At a height of 50 miles the atmosphere is extremely rare; but even at 100 miles it is still dense enough to bring fast-moving meteors to incandescence by friction with the air.

Air is a mixture. The writings of Leonardo da Vinci and some of the ancient Chinese contain references to an active and an inactive constituent of the atmosphere; but the chemical investigators of the latter half of the eighteenth century were the first to demonstrate clearly the composite character of the atmosphere. The task was not fully completed until the closing years of the nineteenth century. A few simple experiments will convince us that air is composed of several different substances.

Water vapor. The evaporation of water and the condensation of moisture on cold objects suggest the presence of water vapor in the atmosphere. The moisture content of a given volume of air may be determined by passing the air through a cold trap, in which the water condenses or may even freeze. Also, the air may be passed through a tube containing some material such as calcium chloride (Fig. 70, p. 111), which readily combines with and retains water vapor. The increase in weight of such a tube is a direct measure of the weight of water vapor present in the sample of air.

Carbon dioxide. When carbon dioxide is bubbled through a clear solution of calcium hydroxide ($\text{Ca}(\text{OH})_2$), a white precipitate of calcium carbonate is formed, and this reaction serves as a good test for the gas:



In this way one can prove the presence of carbon dioxide in the air, as well as in one's breath.

NOTE. When two substances in solution react to form an insoluble compound (or element), which therefore settles out, or *precipitates*, the sign \downarrow is placed by the side of the formula (or symbol) of the precipitate (see equation above).

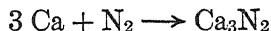
The percentage of carbon dioxide present in any sample of *dry* air is easily determined by passing a definite volume of the air through a tube containing soda lime (a solid mixture of sodium hydroxide and calcium hydroxide). The tube and contents are weighed both before and after the air is passed through the tube. The soda lime removes from the air all the carbon dioxide pres-

ent, so that the increase in the weight of the tube and contents equals the weight of carbon dioxide in the air passed through the tube.

Oxygen and nitrogen. If a substance whose product of combustion is a solid is burned in a confined volume of air, the volume will decrease by about one fifth. This experiment may be conducted in the following manner: A piece of phosphorus, held by a wire, is ignited and is immediately covered with a vessel (containing air) inverted over water. The phosphorus combines with the oxygen to form an oxide, P_4O_{10} , called phosphorus pentoxide. This is a white powdery solid which floats about in the air, but soon settles and is dissolved by the water. The removal of the oxygen is indicated by the rising level of water (Fig. 101).

The gas which remains (largely nitrogen) exhibits characteristics different from those of the original air: it does not support combustion, it is much less reactive than air, and it is incapable of supporting life.

Argon and other gases. The demonstration of the presence of the other constituents of the atmosphere is somewhat more difficult. It is necessary to free a sample of dry air, first, of its oxygen and carbon dioxide (as above), and then of its nitrogen. The latter operation is complicated not only by the large amount of nitrogen relative to the other remaining constituents but also by the sluggish reactivity of the nitrogen. On a small scale, the nitrogen may be removed by passing the gas sample over heated calcium, with which the solid, calcium nitride, is formed:



The volume of gas remaining after such a series of operations, while definite in amount, is very small (less than 1 per cent of the total sample of air). This gas consists of argon mixed with minute percentages of the elements helium, neon, krypton, and xenon. These elements resemble nitrogen in many ways but differ from it in that they are completely inert toward chemical reagents.

Fractional distillation. Because of the extreme chemical inertness of the rare gases, helium, neon, argon, krypton, and xenon, contained in this residue of air, physical methods must be used for

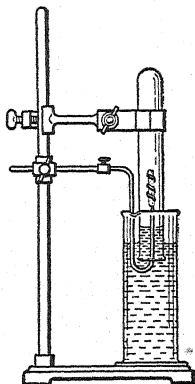


FIG. 101. *Removing the Oxygen from Air by Using Phosphorus*

their separation. It is possible to achieve some substantial separation by taking advantage of the different rates of diffusion, that is, by allowing these gases to diffuse through a porous wall — for example, through porous clay. But a far more effective and more practical method is *fractional distillation*, which makes use of the difference in *boiling points* of the constituents of the mixture.

In order to have a very large quantity of starting material, liquid air itself (after water vapor and carbon dioxide have been removed) is distilled. It is placed in a suitable vessel and allowed to vaporize. The most volatile substances (those of lowest boiling point) evaporate first, and the least volatile last. The successive vapors in the volatility series are not entirely pure, as they have mixed with them, to some extent, the vapors of the more as well as of the less volatile substances; in other words, the separation is not clean-cut on first distillation. But the vapors may be collected separately, recondensed, and further purified by repeated distillations. The process just described is called *fractional distillation*.

Composition of air. By the various methods, both chemical and physical, just described, it is possible to separate the mixture air into its various constituents and to measure quantitatively their amounts in a sample of air.

Composition of Dry Air

NAME	BOILING POINT IN DEGREES CENTIGRADE	BY VOLUME	BY WEIGHT
Nitrogen	− 195.8°	78.03 per cent	75.46 per cent
Oxygen	− 182.96°	20.99 per cent	23.20 per cent
Argon	− 185.8°	0.94 per cent	1.28 per cent
Carbon dioxide		3–4 in 10,000	0.045 per cent
Hydrogen	− 252.5°	1 in 10,000 (?)	
Neon	− 246.3°	1 in 65,000	1 lb in 44 tons
Helium	− 268.98°	1 in 200,000	1 lb in 725 tons
Krypton	− 152.9°	1 in 1,000,000	1 lb in 173 tons
Xenon	− 107.1°	1 in 11,000,000	1 lb in 1208 tons
Water vapor	Variable within wide limits		

The constancy of the composition of air. Notwithstanding the changes constantly taking place which tend to alter the composition of air, the results of many analyses of *dry* air collected in the open fields show that the percentages of oxygen and nitrogen, as well as of carbon dioxide, are very nearly constant, not only from

place to place, but from year to year. This constancy of composition in the case of oxygen is shown in the following analyses tabulated by Clarke. The percentages are expressed in volumes.

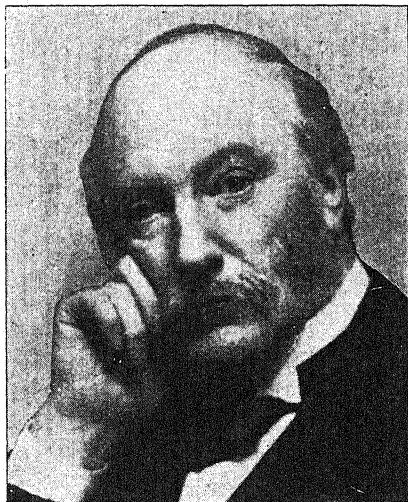
LOCALITY OF SAMPLES	NUMBER OF ANALYSES	MINIMUM OXYGEN	MAXIMUM OXYGEN
Paris	100	20.913	20.999
Heidelberg	28	20.840	20.970
Manchester	32	20.780	21.020
Mountains of Scotland	34	20.800	21.180
Dresden	46	20.877	20.971
Cape Horn	20	20.72	20.970
Cleveland, Ohio	45	20.900	20.950

We do not know in detail why the composition of the air remains constant. Certainly the balance sheet embraces those processes by which gases are added to the atmosphere and those others by which they are taken away. Carbon dioxide is poured into the atmosphere, and oxygen withdrawn, by respiration, decay of organic matter, and combustion — forest fires and the burning of immense quantities of coal, wood, and oil. From these various sources as much carbon dioxide is furnished to the atmosphere every few years as is already present. On the other hand, the weathering of the rocks removes carbon dioxide in vast amounts, and growing plants not only remove carbon dioxide *from* but also give oxygen *to* the atmosphere. Perhaps all these opposing processes tend to offset each other. But it is very likely that the equilibrium exchange of gases between the atmosphere and the sea has a great deal to do with maintaining the constancy of the composition of the atmosphere.

Since we can obtain individual samples of all the substances present in air, let us examine them and study their properties and behavior. (Oxygen has already been treated in Chapter 6, and water will be discussed in Chapter 10.)

THE RARE GASES IN THE ATMOSPHERE: HELIUM, NEON, ARGON, KRYPTON, XENON

Because of the minute percentages of these elements in the atmosphere, and also because of the similarity in properties between them and nitrogen, they were not discovered until comparatively recent years. They resemble nitrogen in that they are colorless, odorless, tasteless gases and very difficult to liquefy. *They are*



Elliott & Fry

FIG. 102. *Lord Rayleigh (John William Strutt) (1842-1919)*

Cavendish Professor of Physics at Cambridge University, and professor of natural philosophy at the Royal Institution of Great Britain. An accomplished investigator along many lines of physical research. His interest in Prout's hypothesis led him to study gas densities and to detect the difference in density of nitrogen from air compared with that from chemical sources. In association with Ramsay, these studies resulted in the discovery of argon. He received the Nobel prize in 1904



Elliott & Fry

FIG. 103. *Sir William Ramsay (1852-1916)*

Eminent Scottish chemist; professor of chemistry in University College, London, until 1913, when he retired. Ramsay and Lord Rayleigh, working together, discovered argon in 1894. Together with Travers, Ramsay also discovered neon, krypton, and xenon, and was the first to show that helium is a constituent of the atmosphere. For these remarkable discoveries he was awarded the Nobel prize for chemistry in 1904

characterized by their chemical inertness. Although they have been subjected to the action of many other substances under conditions which have been most favorable for effecting the combination of elements, no one has yet succeeded in preparing any compounds of these elements (with the possible exception of a chloride of krypton, unstable hydrates of argon, krypton, xenon, and particularly compounds of argon with boron trifluoride, notably $A \cdot 2 BF_3$).

Historical. Argon. The first evidence for the existence of the inert gases in the atmosphere was obtained by Cavendish. In 1785, in the course of his experiments on air, he passed electric sparks through an enclosed volume of air (nitrogen and oxygen), introducing more oxygen from time to time, so as to make certain that the quantity of oxygen present should be sufficient to combine with all the nitrogen. After repeated sparking, the

oxides of nitrogen formed by the union of the gases, together with the excess of oxygen, were removed by absorbing them in appropriate liquids. In this experiment Cavendish observed that even after repeated trials there always remained a small residue of gas, in volume about $\frac{1}{120}$ of the air taken, which would not combine with oxygen and therefore presumably was not nitrogen.

No attention was paid to this observation until 1892, when Lord Rayleigh (Fig. 102) observed that 1 l of nitrogen prepared from its compounds was lighter by about 5 parts in 1000 than the same volume prepared from air. He repeated his experiments many times, always with the same results. Finally he and Sir William Ramsay (Fig. 103), working together, showed that there was indeed a residue of extremely inert gas in nitrogen from air. This gas was named *argon* ("lazy one") because of its inert character.

Helium. In 1889 the American chemist Hillebrand found that certain minerals containing the element uranium evolve a gas when heated. After a brief investigation he concluded that the gas so evolved was nitrogen. In 1895, shortly after the discovery of argon, the attention of Ramsay was called to this experiment, with the suggestion that argon might be present in the gas which Hillebrand had obtained. Ramsay repeated the experiment, obtained the gas, and studied its spectrum. Some of the lines of this spectrum corresponded to no known element on the earth. Strangely enough they did correspond to some lines found by the French astronomer Janssen in 1868 in the spectrum of the corona of the sun and attributed by Lockyer to an unknown element, *helium*, in the atmosphere of the sun. Shortly after the identification of helium in the gases evolved on heating uranium minerals, Ramsay was able to obtain the gas in fairly pure state and study its properties. Since that time helium has been found to be a constituent of our own atmosphere, of the gases from certain springs, and of natural gas in certain regions of Texas and elsewhere.

Neon, krypton, and xenon. Following the discovery of argon and helium an exhaustive examination of various gases was made, especially of those obtained from minerals, in the hope that still other elements might be discovered. These investigations proved fruitless until finally directed to liquid air as a possible source of such unknown elements. Large quantities of liquid air were subjected to careful fractional distillation, and the different fractions examined with the spectroscope for the presence of unknown elements. By this method Ramsay and Travers, in 1898, succeeded in isolating three additional elements, which were named *neon*, *krypton*, and *xenon*, meaning, "new," "hidden," and "stranger."

In an effort to discover still other elements in air, Moore examined the gases, first from 19 tons and later from 100 tons of liquid air, but found no new elements.

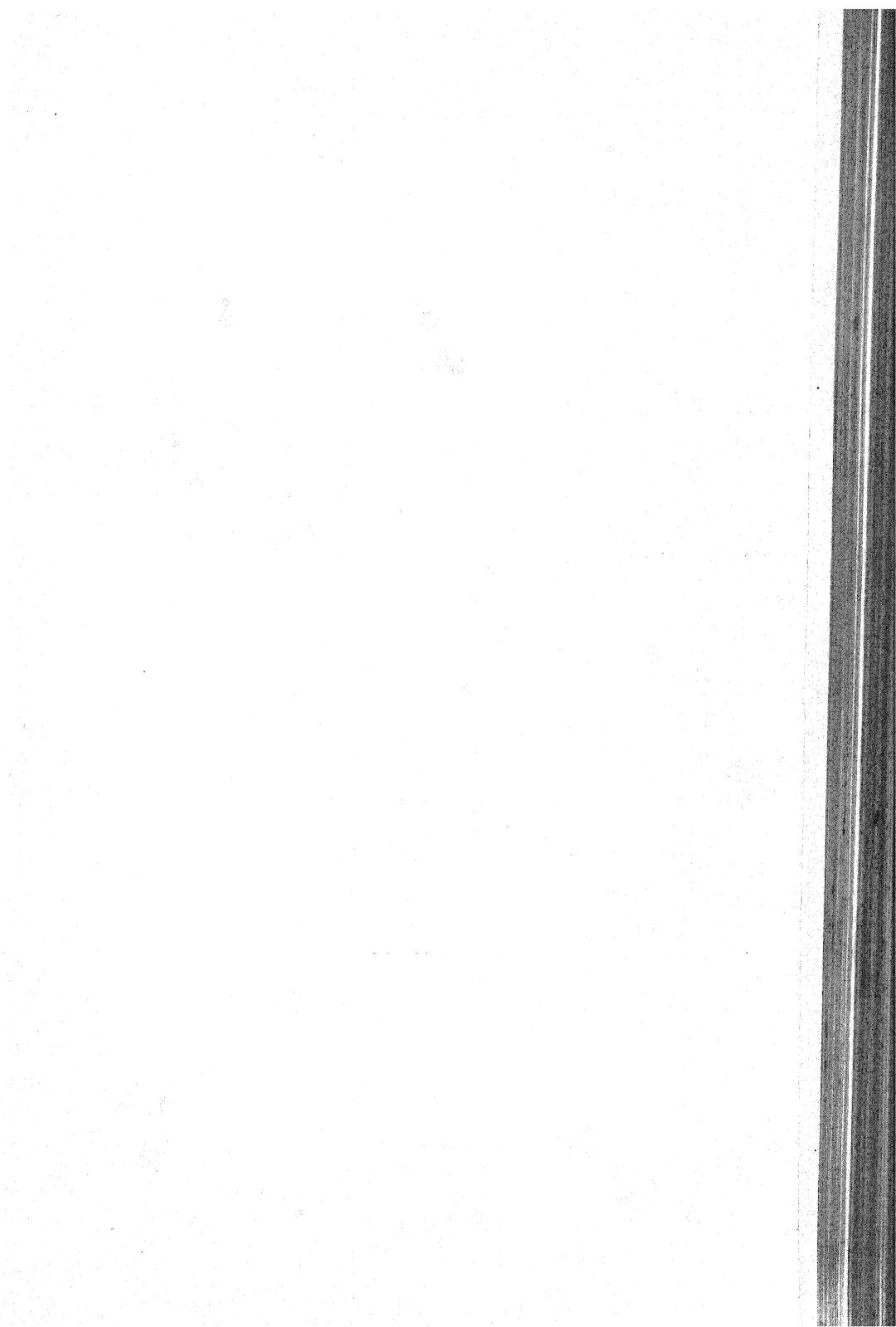
Uses of the rare gases. (1) Helium is about twice as heavy as hydrogen, but has 92.6 per cent of the lifting power of hydrogen.

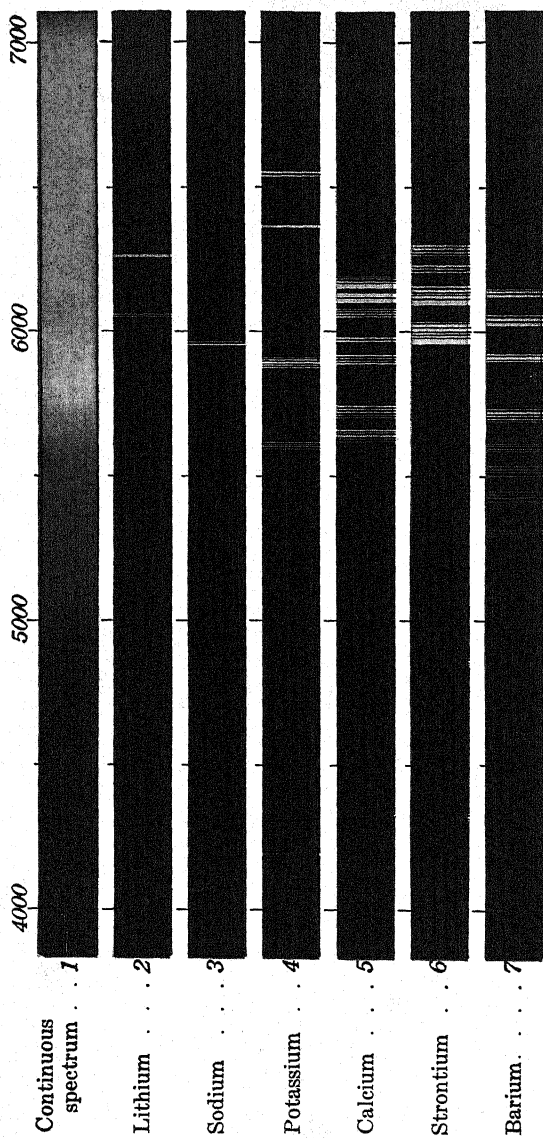
The use of helium in the inflation of balloons and other lighter-than-air craft is especially desirable because it will not burn. The Federal government maintains a plant in Texas to recover large quantities of helium from natural gas. In the recovery process advantage is taken of the low boiling point of helium (-268.9°). This gas, which in 1918 cost \$2500 per cubic foot, is now prepared at only a few dollars per thousand cubic feet. (2) Workers in caissons and diving bells suffer from the "bends," a condition brought on by nitrogen which dissolves in the blood (in the lungs) at the high pressure. No harm is done if the affected person passes through a "decompression chamber"; but the nitrogen escapes as bubbles in the blood, which block circulation, if the transition from high to normal pressure is made too rapidly. An artificial atmosphere of oxygen and helium greatly lessens the danger because of the extremely low solubility of helium. (3) By evaporating liquid helium under reduced pressure, a temperature of -272.3° has been reached. Still lower temperatures have been attained (to within about 0.001° of the absolute zero) by other physical methods which involve the use of liquid helium. (4) Neon signs consist of glass tubes of the desired forms, containing neon gas, at reduced pressure, through which an electric discharge passes. Sometimes a certain percentage of argon or helium (or both) is added to give a different color; and sometimes mercury is also introduced. (5) Argon is now extensively used in gas-filled electric filament lamps, which are more efficient than the older type filled with nitrogen.

Some of the main facts about these inactive gases are given in the following table:

	HELIUM	NEON	ARGON	KRYPTON	XENON
Weight of 1 l in grams . . .	0.1785	0.900	1.782	3.708	5.851
Weight of 22.4 l	4.0	20.2	39.9	83.1	131.1
Atomic weight	4.003	20.183	39.944	83.7	131.3
Number of atoms per molecule	1	1	1	1	1
Number of cubic centimeters dissolved by 1 l of water at 20° and 760 mm pressure .	13.8	14.7	37.9	73.	110.9
Boiling point of liquid form .	-268.9°	-246.3°	-185.8°	-152.9°	-107.1°
Melting point of solid form .	-272.2°	-248.67°	-189.2°	-169.0°	-140°

The spectroscope. When a beam of light passes through a triangular prism of glass, it is bent out of its course and emerges at a decided angle with its original direction, as shown in Fig. 104. Ordinary light is made up





A CONTINUOUS SPECTRUM AND SIX BRIGHT-LINE SPECTRA

These seven colored bands are typical of the many that may be seen in the spectroscope. Number 1, called a *continuous* spectrum, is an unbroken gradation of colors ranging from violet to red, and is seen when a spectroscope is directed at a solid body heated to incandescence. The others are *bright-line* spectra and are examples of what is seen in the spectroscope when various elements (or their compounds) are vaporized in a Bunsen flame or in an electric arc, each spectrum being characteristic of some one element. The numbers at the top refer to the wave lengths of the light, measured in suitable units

of waves of many different lengths, and each one is deflected, or *refracted*, to a different degree, so that the various colors corresponding to the differ-

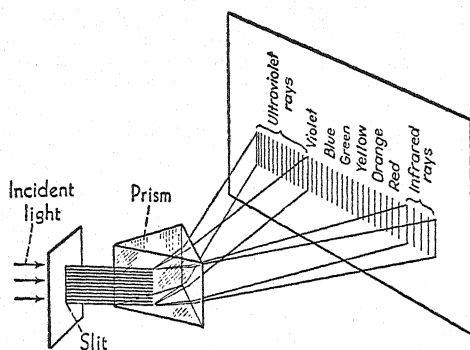


FIG. 104. *The Separation of White Light into its Constituents*

ent wave lengths are spread out in a *spectrum* (opposite this page). The red is the least refracted, the violet the most. A beam of *white* light from an incandescent solid gives a *continuous spectrum* of colors from red through orange, yellow, green, blue, to violet. The spectrum of any *colored* light is not necessarily continuous, but shows merely those colors of which the light is composed.

Fig. 105 represents a spectroscope, an instrument invented by Bunsen and Kirchhoff in 1860 for viewing a spectrum. If we allow light, say from a colored flame, to enter the slit *B*, and if we look into the eyepiece of telescope *A*, the spectrum of the flame is seen as a series of bright lines (images of slit *B*). The lines are seen against the background of a wave-length scale in *C*, which is visible to the eye at the same time.

Emission spectra. A glowing gas or vapor gives an interrupted, or *bright-line*, spectrum, as a rule characteristic of the *elements* present rather than of any compound. Even a slightly volatile solid, if heated sufficiently in a flame or spark, can be brought to a point where its vapor will emit light. A simple way to produce a *flame spectrum* is to dip a platinum wire into some of the substance or a concentrated solution of it, and heat it in a Bunsen flame. The flame takes on the color of the glowing vapor of the substance. When a higher temperature is

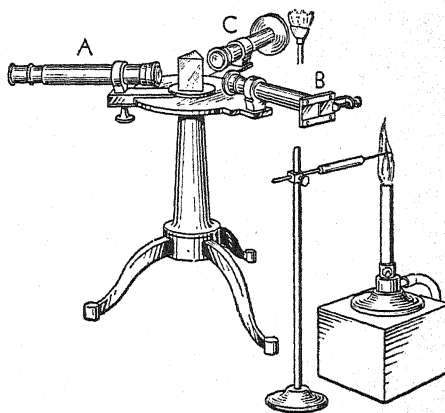


FIG. 105. *Diagram of a Simple Spectroscope*

desired, a little cavity may be hollowed out in the lower carbon of an arc light, and some of the substance placed in this. A so-called *arc spectrum* is then obtained. Metallic substances may be made to form a spark gap for an induction-coil discharge, to give a *spark spectrum*. Or, when a gas at a suitably low pressure is sealed within a tube provided with electrodes (known as a Plücker tube, Fig. 106) and excited with an electric discharge from the induction coil, the gas becomes brilliantly luminous.

All these methods for producing spectra are extensively employed in analytical procedure, for identification of elements, and for the detection

of elements which may be present in a given sample of material in extremely minute traces. Several of the elements have been discovered by finding spectral lines which had not previously been identified as characteristic of any known element.

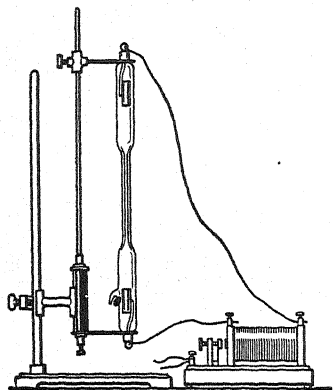


FIG. 106. *Plücker Tube for Showing Vacuum-Tube Spectra*

Absorption spectra. It has been previously stated that an incandescent solid gives a continuous spectrum. If a layer of gas is interposed between the incandescent solid and the prism, the gas will absorb those wave lengths of light which it can itself give out when luminous, and the continuous spectrum will be interrupted by a series of *black lines* corresponding to the bright lines of the gas. These black lines are known as *absorption lines*, and a spec-

trum in which they appear is called an *absorption spectrum*. In this way the solar spectrum is crossed by a great number of dark lines due to the presence of gases in the envelope surrounding the incandescent center of the sun. The absorption lines in the solar spectrum are called *Fraunhofer lines*, after their discoverer. We have learned much about the elements present in the sun's atmosphere from a study of its absorption spectrum.

Liquids, solids, and solutions also give absorption spectra, and their study has yielded much important information about the chemical structure of the molecules absorbing the light.

NITROGEN

Occurrence. In the free condition nitrogen makes up about four fifths of the atmosphere, as we have already seen. In the combined state it is present in sodium nitrate (NaNO_3) and potassium nitrate (KNO_3), and in ammonia (NH_3) and its compounds. Nitrogen is likewise an essential constituent of proteins and many other "organic" compounds which are present in living organisms. The human body contains about 3 per cent of nitrogen.

Preparation of nitrogen from air. For commercial purposes nitrogen is obtained entirely from liquid air by fractional distillation (p. 139). In the laboratory it can be prepared by bringing air into contact with some substance that will combine with the oxygen but not with the nitrogen. The substances ordinarily used are phosphorus (Fig. 101) and copper (Fig. 107), because they combine

readily with the oxygen and because the oxides formed are *solids* and so admit of an easy separation from the remaining nitrogen. This slightly impure nitrogen, containing about 1 per cent of the rare gases, may be used for a study of most of the properties of the ele-

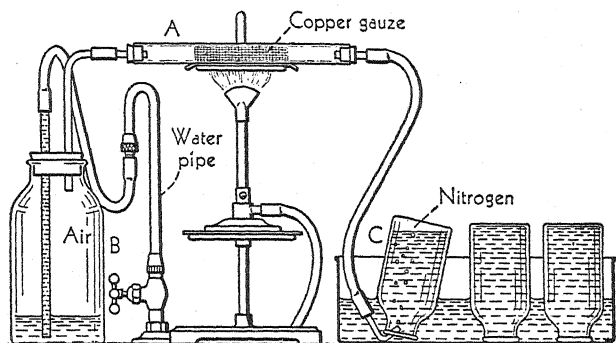
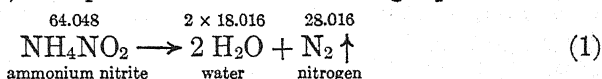


FIG. 107. *Preparing Nitrogen by Passing Air over Hot Copper*

The metal in the form of gauze is placed in a tube *A* and heated to a high temperature. The air is then forced slowly through the tube by allowing a small stream of water to flow into a bottle *B* connected with the tube, as shown in the figure. The oxygen combines with the hot copper and forms copper oxide (CuO), a solid which remains in the tube while the nitrogen passes on and is collected over water in the bottles *C*

ment, since these are not materially affected by the presence of the other gases. The method best adapted for preparing *pure* nitrogen in the laboratory consists in liberating the element from some of its compounds.

Preparation of nitrogen from compounds. The compound that is most frequently used for the preparation of nitrogen is ammonium nitrite (NH_4NO_2). When heated, this compound decomposes into nitrogen and water, as represented in the following equation :



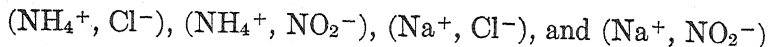
Since ammonium nitrite is an unstable solid, it is convenient to substitute for it a mixture of sodium nitrite (NaNO_2) and ammonium chloride (NH_4Cl). In solution these two compounds react to form sodium chloride and ammonium nitrite :



As fast as it is formed, the ammonium nitrite decomposes into nitrogen and water, in accordance with equation (1).

The term *ammonium*, used in the names of such compounds as ammonium chloride, is applied to the covalent group of atoms NH_4

which is present in these compounds. It is an ion, positively charged, and is called an *ammonium ion*. Both ammonium chloride and ammonium nitrite, as well as sodium chloride and sodium nitrite, are electrovalent compounds:



Properties of nitrogen. Like hydrogen and oxygen, nitrogen is a colorless, odorless, tasteless gas. It is slightly lighter than oxygen; 1 l of it weighs 1.2506 g. Like oxygen and hydrogen it is only slightly soluble in water: 100 cc of water dissolves 2.33 cc of the gas under standard conditions. Liquid nitrogen boils at -195.8° and has a density of 0.8 at its boiling point. At low temperature and under high pressure, it is obtained in the form of an icelike solid which melts at -209.8° (Fig. 108).

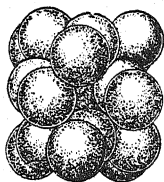


FIG. 108. *Structure of Solid Nitrogen Crystals, Showing Molecules Consisting of Two Atoms*

Chemical conduct. Nitrogen is much less active than oxygen, showing little or no tendency to combine with any other elements at ordinary temperatures. At high temperatures and under suitable conditions it combines with many of the elements. Thus, under the action of electric sparks or when it is heated in the presence of suitable catalysts, nitrogen combines with hydrogen to form *ammonia* (NH_3), and with oxygen to form *nitric oxide* (NO). Nitrogen likewise combines directly with silicon, boron, titanium, and with a number of the metals, notably lithium, magnesium, and calcium. The compounds formed by the union of nitrogen with another element are in general called *nitrides*, just as the compounds formed by the union of oxygen with another element are called *oxides*.

The assimilation of nitrogen. While nitrogen is a very important constituent of the human body, and while we are constantly immersed in a vast sea of this element (weighing more than 20,000,000 tons to each square mile of the earth's surface), nevertheless our bodies are not able to assimilate directly this free nitrogen in the atmosphere, but must obtain their supply from the nitrogenous compounds present in such foods as milk, eggs, meat, beans, and peas. Plants do somewhat better, for some of them are able, by indirect means, to utilize the free nitrogen of the atmosphere.

Uses of nitrogen. The chief commercial use of free nitrogen is in the preparation of *ammonia* (NH_3) by direct combination with hydrogen; the ammonia, in turn, is used in the manufacture of fertilizers and other compounds of nitrogen, especially nitric acid

(HNO_3), which is necessary for the production of explosives, photographic films, and lacquers. In smaller amounts nitrogen is used in the manufacture of other compounds, especially one called *cyanamide*, and for hardening steel. It is also used for filling the space in the capillary over the mercury in thermometers designed for use at temperatures ranging from 300° to 500° .

CARBON DIOXIDE

The oxides of carbon. The element carbon forms three oxides, carbon monoxide (CO), carbon suboxide (C_2O_3), and carbon dioxide (CO_2). Carbon dioxide is the most common, and is discussed at this time because it is present in the atmosphere. Carbon monoxide will be treated later.

Occurrence of carbon dioxide. Carbon dioxide gas is found in open air to the extent of about 3 parts in 10,000, a little higher in cities and a little lower in the country. This apparently small percentage is of fundamental importance in nature; for while the *percentage* of carbon dioxide in air is small, the *total amount* in the atmosphere is very large. In some localities it escapes from the earth in great quantities, and this is especially true of the oil-well and gas-well districts of Mexico and of some Western states. Many spring waters contain it in solution; when such waters reach the surface of the earth, the pressure upon them is diminished and the gas escapes as small bubbles (*effervescence*). Carbon dioxide is a product of the oxidation of all organic matter, and is therefore formed in all ordinary processes of combustion as well as in those of decay. It is exhaled from the lungs of all animals in respiration, and is a product of many fermentation processes, such as that which takes place in the manufacture of alcoholic liquors.

Carbon dioxide in breath. According to Little, carbon dioxide "is normally present to the extent of about 4.5 per cent in human breath, and in a long life a man may exhale more than 20 tons of the gas. For the conduction of the process which results in its production, nature provides the average man with a lung area of about 100 sq yd," or enough for the floor space of a large room.

Properties. Carbon dioxide is a colorless, practically odorless gas 1.5 times as heavy as air. One liter of it weighs 1.9768 g. Its high density compared with that of air may be inferred from the fact that it can be siphoned or poured like water from one vessel downward into another, as shown in Fig. 109. At 15° , and under

ordinary pressure, 1 volume of water dissolves about 1 volume of the gas. Its solubility increases regularly *in proportion to the pressure* until about 5 atm is reached ; beyond this point its solubility increases less rapidly. It is readily obtained in the liquid as well as the solid state.

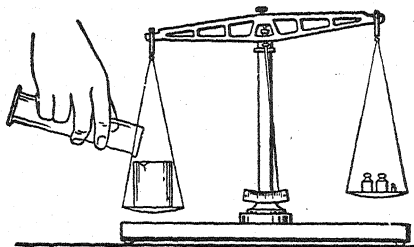
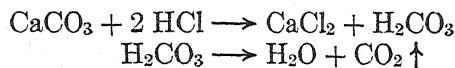


FIG. 109. *Illustrating a Method for Showing that Carbon Dioxide Is Heavier than Air*

Preparation of carbon dioxide.

In the laboratory, carbon dioxide is prepared by the action of an acid, usually hydrochloric, upon calcium carbonate (CaCO_3), which occurs abundantly in nature in the form of limestone and

marble. The latter, being nearly pure calcium carbonate, is more frequently used. When hydrochloric acid is added to marble, calcium chloride (CaCl_2) and the very unstable compound called carbonic acid (H_2CO_3) are formed. This acid at once decomposes into water and carbon dioxide. The latter, being but sparingly soluble, escapes and may be collected by displacement of air or water. The equations for the reactions are as follows :



The apparatus represented in Fig. 110 is convenient and automatic. When the stopcock *D* is opened, the acid runs down into *C* and up into *A*, where it comes in contact with the lumps of marble. The carbon dioxide generated escapes through *D*. If now the stopcock is closed, the gas, being unable to escape, collects in *A* and pushes the acid away from the marble, down into *C* and up into *B*, so that the action ceases until the stopcock is again opened. This apparatus is known as a Kipp generator.

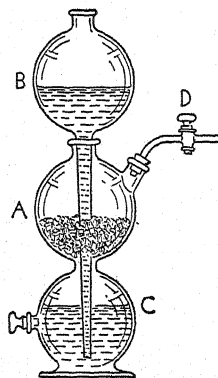
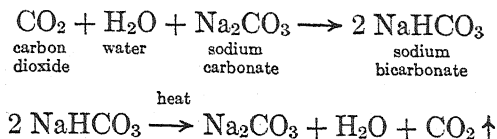


FIG. 110. A Kipp Generator

Preparation for commercial purposes. For commercial purposes carbon dioxide is obtained from a number of sources. (1) The chief source is the combustion of coal. The products of combustion are sprayed with a solution of sodium carbonate, which reacts with the carbon dioxide in the gases to form the compound known as sodium bicarbonate. The latter compound, when

heated, evolves pure carbon dioxide and reverts to sodium carbonate, which can then be used over again.



(2) Another source of carbon dioxide is in the preparation of hydrogen by passing steam over carbon in the presence of a catalyst (p. 106). The carbon dioxide is separated from the hydrogen by passing the mixture into water under pressure. The carbon dioxide gas is dissolved by the water and is recovered by relieving the pressure on the solution. (3) The gas is also formed in the manufacture of lime and in certain kinds of fermentation (see manufacture of lime and of ethyl alcohol), and these processes serve as minor sources of the gas. (4) It is obtained directly from certain gas wells, especially in Mexico.

Production and costs. It will be observed that in these sources of carbon dioxide the processes are not carried out primarily for the purpose of securing the gas. It is formed in the combustion of coal and in the manufacture of certain compounds, and if not utilized would go to waste. Naturally attempts would be made in all such cases to find an economical method of separating the gas, and some of these have been successful. In other cases the cost of recovery may be greater than the cost of preparing the desired compound by a special process. After all, it is the cost which determines the selection of the method used in the preparation of any compound on a large scale for commercial purposes.

Liquid and solid carbon dioxide. At ordinary temperature (20°) carbon dioxide is liquefied by a pressure of 56.3 atm. Liquid carbon dioxide is colorless and slightly lighter than water. The liquid dissolves some organic substances, such as naphthalene and camphor, but only a few inorganic substances. The commercial carbon dioxide, compressed in steel cylinders, is under such great pressure that it is largely in the liquid state. When the pressure is released, the rapid evaporation of the gas reduces the temperature sufficiently to freeze a portion of the escaping liquid to a snowlike solid.

Under ordinary atmospheric pressure this solid passes directly into a gas without melting and sublimates at -78.5° . Solid carbon dioxide is now produced on a large scale in nearly all countries, from both natural and artificial sources, for use as a refrigerant.

Preparation of solid carbon dioxide. Solid carbon dioxide may be purchased almost anywhere under the trade name "Dry Ice." It is easily prepared from the commercial cylinders of the compressed gas. The cylinder should be placed across a desk and supported in such a way that the end provided with a valve is several inches lower than the other end. A loose bag is made by holding the corners of a piece of cloth tightly around the neck of the valve (Fig. 111); and when this is opened, the liquid, together with the gas formed by its rapid evaporation, rushes out. The absorption of heat by the evaporation freezes a portion of the liquid, and the solid is strained out from the gas by the cloth and collects in the bag.

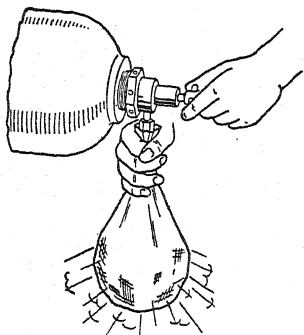
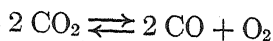


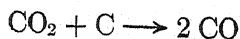
FIG. 111. Preparation of Solid Carbon Dioxide

The very low temperature of this snow may be inferred from the ease with which it freezes mercury. A filter paper is placed in the bottom of a small evaporating dish, and some mercury is poured upon it. One end of a piece of wire is wound into a flat coil and dipped into the mercury. A quantity of the solid carbon dioxide is placed upon the mercury and from 10 to 15 cc of ether poured over it. In this way a temperature of -100° may be obtained, so that the mercury solidifies (freezing point -38.9°) in a minute or two and may be removed from the dish by the wire, which serves as a handle. While the solid carbon dioxide is intensely cold, it may be handled without much danger, because the skin is protected from direct contact with it by a layer of evaporated gas.

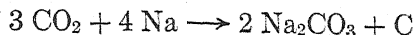
Chemical conduct. Carbon dioxide is a very stable substance. At high temperatures partial decomposition takes place, as indicated in the following equation:



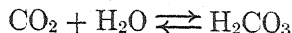
At 2000° , under a pressure of 6 atm, about 5 per cent of the carbon dioxide is thus decomposed. It will not combine with oxygen and is therefore incombustible; neither will other substances burn in it under ordinary conditions, for although it contains a large percentage of oxygen, this is held in very firm combination. A few energetic reducing agents remove at least a part of its oxygen. Thus, if it is passed over carbon at temperatures above 1000° , the gas is partially reduced, forming carbon monoxide:



At high temperatures sodium partially reduces carbon dioxide to carbon :

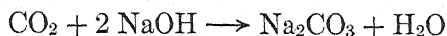


When carbon dioxide is dissolved in water, especially under pressure, part of the dissolved gas combines with the water according to the equation



When the pressure is diminished, the reaction goes in the opposite direction. The product of the reaction, H_2CO_3 , is called *carbonic acid*. It gives the solution a somewhat pungent, or biting, taste.

If carbon dioxide is passed into an aqueous solution of the hydroxide of certain metals, a carbonate of the metal is formed. For example, with sodium hydroxide, the reaction is represented by the following equation :



The resulting compound, Na_2CO_3 , known as *sodium carbonate*, remains dissolved in the water present.

Physiological effect of carbon dioxide. Carbon dioxide is not regarded as a poisonous gas, but experiments show that one cannot breathe air containing more than 10 per cent of the gas longer than ten minutes without losing consciousness. Air containing 20 per cent or more of the gas causes partial or complete closure of the glottis.

On the other hand, carbon dioxide appears to be the stimulant that acts upon the respiratory nerve centers in breathing; the animal breathes in order to eliminate carbon dioxide. On this account carbon dioxide is sometimes added to the oxygen (usually about 7 per cent of the dioxide and 93 per cent of oxygen) used in treating cases of lung disorders, asphyxiation, partial drowning, electric shock, and, in general, suspended breathing due to any cause.

Uses of carbon dioxide. Commercially, carbon dioxide is used chiefly in the manufacture of soda water and similar beverages, as a fire-extinguisher, and in solid form as a refrigerant. Large amounts are also used in the manufacture of sodium bicarbonate (see Solvay process). Ordinary soda water consists of various flavoring extracts to which is added water charged with carbon dioxide under pressure. When the pressure is removed, some of the gas escapes, producing *effervescence*.

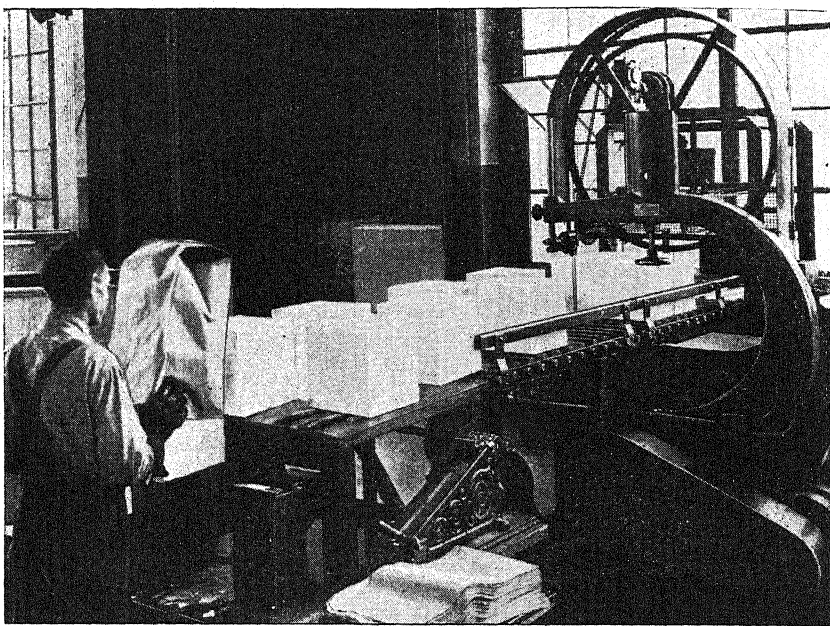
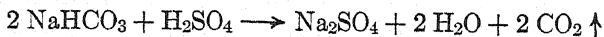


FIG. 112. *Sawing a Slab of Solid Carbon Dioxide (Dry Ice) into Pieces*

Solid carbon dioxide, under the trade name of "Dry Ice" (Fig. 112), has come into favor for the refrigeration of certain foods, especially ice cream. It does not involve the use of sawdust or salt; and it has the advantage of cleanliness, since it evaporates without leaving any residue whatever.

Portable fire-extinguishers. The flame of a burning candle is extinguished in air containing as little as 2.5 per cent of carbon dioxide; for this reason the dioxide is used as a fire-extinguisher.

Two common types of carbon dioxide fire-extinguishers are shown in Figs. 113, 114. That shown in Fig. 113 is a device for generating carbon dioxide under pressure. The liquid is a solution of sodium bicarbonate (ordinary baking soda (NaHCO_3)) in water contained in a metal cylinder. The bottle *A* contains sulfuric acid. In case of fire the apparatus is grasped by the handle *D* and inverted. The stopper *B* drops onto the support *C*, thus allowing the acid in the bottle *A* to flow out into the solution of sodium bicarbonate. The acid at once reacts with the sodium bicarbonate, generating carbon dioxide, thus:



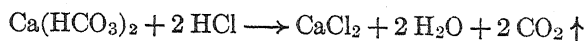
(The arrow pointing up indicates the escape of a gas.) Some of the gas dissolves in the water, while the rest forces the water out through the

nozzle *E*. Although the volume of water so obtained is not large, it is very effective as a fire-extinguisher because of the carbon dioxide accompanying it.

In Fig. 114 the carbon dioxide stored under great pressure is directly used. When the pressure is removed by turning the valve, a fine spray of gaseous and solid carbon dioxide escapes and is directed upon the fire, as shown in the figure.

Amount of carbon dioxide in the atmosphere. At the beginning of this chapter it was shown that the weight of the atmosphere itself is about 5.7×10^{15} tons. By *volume* there are 3 parts of carbon dioxide in 10,000 of air; but by *weight* there are 4.5 parts in 10,000, since a volume of carbon dioxide is about 1.5 times heavier than an equal volume of air. Hence, if we multiply 5.7×10^{15} tons by 0.00045, we find the total weight of carbon dioxide in the atmosphere, namely, about 2.6×10^{12} tons (2,600,000,000,000 tons).

Carbon dioxide in the sea. It is likely that about 0.015 per cent by weight of sea water is carbon dioxide (held combined as bicarbonates). If we could add enough hydrochloric acid to the sea to set free all this carbon dioxide, in accordance with the equation



how would the amount so liberated into the atmosphere compare with the carbon dioxide already present?

To answer this question we first need to know the approximate total weight of the sea. If all the waters of the earth were spread out in an even layer, the depth would be about 10,000 ft, or 300,000 cm. The diameter of the earth is 12,756 km, or $12,756 \times 10^5$ cm, and the total area of the earth is $\pi(12,756 \times 10^5)^2$, or about 5.1×10^{18} cm². This area multiplied by the depth gives the volume (in cubic centimeters) of such a shell of sea water: 5.1×10^{18} cm² \times 3×10^5 cm = 1.5×10^{24} cc. Assuming, for the sake of simplicity, that the density of sea water is about 1, we then have 1.5×10^{24} g as the total weight of the sea!

Of this, 0.015 per cent is carbon dioxide: 1.5×10^{24} g \times 0.00015 = 2.3×10^{20} g of carbon dioxide. Reduced to metric tons, this would be $2.3 \times 10^{20} \div 10^6 = 2.3 \times 10^{14}$, or about 2.53×10^{14} tons (of 2000 lb). Now

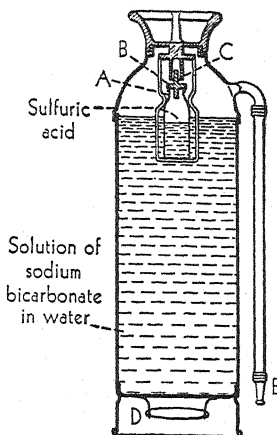


FIG. 113. A Fire-Extinguisher in Which Water and Carbon Dioxide Are Used to Extinguish Flames

let us compare this with the weight of carbon dioxide in the atmosphere, namely, 2.6×10^{12} tons. It is about 100 times (10^2) as great. In other

words, if we could liberate the carbon dioxide of the sea, our atmosphere would contain about 100 times as much carbon dioxide as at present. From what was stated previously, under the section "Physiological effect of carbon dioxide," it will be realized that men could not live comfortably in such an atmosphere.



Walter Kiddle and Company

FIG. 114. A Form of Fire-Extinguisher

A fine spray of gaseous, liquid, and solid carbon dioxide escapes from the metal cylinder, where the gas is stored under great pressure

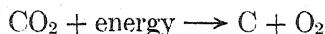
Quantity of carbon dioxide formerly present in the atmosphere.

A large percentage of the carbon dioxide of the sea undoubtedly at one time *did exist* in the atmosphere. On the basis of the known carbonate deposits, principally limestone beds, in the earth's crust, it has been estimated that there was probably enough carbon

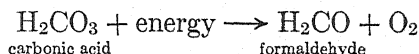
dioxide present in the atmosphere to give a pressure of many atmospheres. At such high pressures the carbon dioxide, with the aid of water, attacked the bare granites and other igneous rocks, and combined with the lime (CaO) in these rocks to form calcium carbonate (CaCO_3). This was deposited directly as a sedimentary limestone or, after being carried in solution in river water to the sea, was there laid down in enormous beds made of the calcareous remains of shell-forming organisms. Thus, largely through the intervention of these carbonate-producing reactions, on a vast scale, by land and sea, over hundreds of millions of years, the atmosphere's content of carbon dioxide was diminished to what we know it to be at the present time. Even today, with much of the earth's rock

surface covered over with a protective mantle of vegetation, and with the effective concentration of carbon dioxide only 3 parts in 10,000 of air, it has been estimated (by Chamberlain) that about 1,620,000,000 tons of carbon dioxide are withdrawn annually from the atmosphere by the chemical attack on the rocks.

Photosynthesis. But not all the carbon dioxide which disappeared from the atmosphere was removed by the weathering of the rocks. Plants eventually began to grow, and they grew most luxuriantly under the hothouse conditions of those old times, millions of years ago. *Plants consume carbon dioxide.* The leaf of a plant is a chemical factory where sunlight, in the presence of water and in the presence of the complex substance *chlorophyll*, is able to bring about the decomposition of carbon dioxide into carbon and oxygen:



Or perhaps it is carbonic acid (H_2CO_3) which is decomposed into formaldehyde and oxygen:



At any rate, oxygen is liberated, and carbohydrates (sugars and starches) of the general formula $(\text{H}_2\text{CO})_x$ are formed.

The decomposition reaction in which oxygen is liberated is *endothermic*, and the energy required to make the reaction proceed is supplied by the sunlight. The energy-traps which catch and remove the energy from the incident beam of sunlight are probably the chlorophyll molecules. Most of the energy which they receive is taken from the reddish-orange region of the spectrum (see the colored plate facing page 145). When reddish-orange light is absorbed from white light, the remaining light takes on the complementary color, green. That is why chlorophyll is green.

The chlorophyll is contained in the chloroplasts (Fig. 115), which, in vast numbers, are located mostly in the palisade cells near the upper surface of the leaf, where the sunlight strikes. The area of the leaf surface of a tree may be very large; for instance, an elm tree of average size has about 7,000,000 leaves and about 5 acres of leaf surface. The carbon dioxide, from the air, enters the leaf through mouths, or

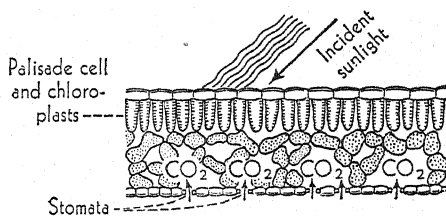


FIG. 115. Magnified Section of a Leaf

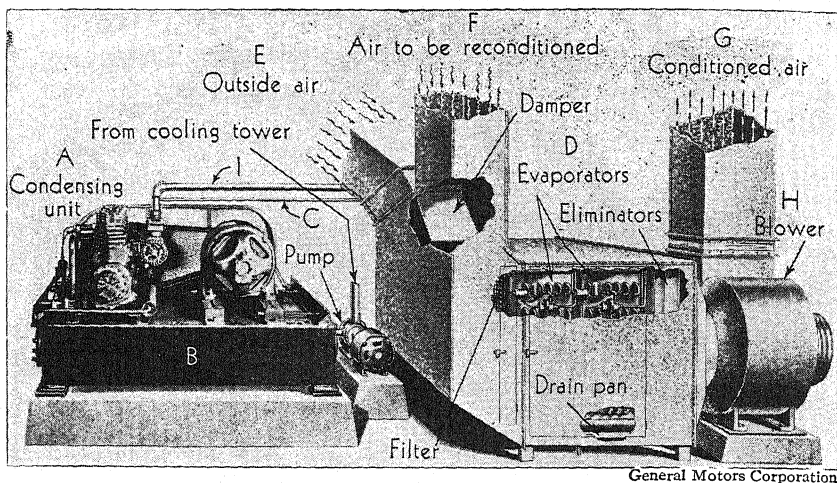


FIG. 116. *A Form of Air-Conditioning Apparatus. It Operates on the Same Principle as the Mechanical Household Refrigerator*

A set of tubes is filled with an easily condensed gas. This gas is liquefied by pressure in the condensing unit *A*. The heat set free is absorbed by a current of water. The resulting liquid runs into the evaporators *D*, where it vaporizes with absorption of heat that keeps the pipes cold. The incoming air passes over these pipes. The air is thereby cooled, and any excess moisture present in it condenses and collects in the drain pan. The cool, dry air is then forced by the blower *H* through the building

stomata, on the underside of the leaf. Just how the chlorophyll molecules hand on to the molecules of carbon dioxide or carbonic acid the energy which they receive from sunlight is not known.

Importance of photosynthetic process. The importance, in nature, of this chemical reaction may be judged from the following considerations :

1. **Foods.** Animals obtain their organic foods from plants, and plants in turn are dependent on the photosynthesis reaction. Sugars and starches are formed as primary products of photosynthesis ; and the fats, proteins, vitamins, and other such foods are formed, by complex chemical reactions, from the primary products. Indeed, with few exceptions, it seems probable that *all the naturally occurring organic substances* originate directly or indirectly in photosynthesis.

2. **Fuels.** The sunlight energy used up in the decomposition of carbon dioxide in the leaf is stored as chemical energy in the oxygen and in the sugars, starches, and cellulose. All these organic substances are combustible ; and if they are allowed to burn in air, carbon dioxide is re-formed, the reactions are exothermic, and the original energy tapped off from the sunlight is yielded back as heat

of combustion. It is in this sense that we may say that practically all our available energy comes from the sun. Wood (largely cellulose), by a slow process of rotting over a period of many millions of years, has been converted into peat, lignite, and finally coal; and probably oil and natural gas owe their origin to photosynthesis.

3. **Oxygen.** To photosynthesis we may also look for the possible explanation of how our atmosphere got its oxygen. It seems not unlikely that it was set free from carbon dioxide by plants. The total weight of oxygen in the atmosphere is enormous, about $\frac{1}{5} \times 5.7 \times 10^{15}$ tons (p. 137). But if we consider that only about 3 lb of oxygen is present over every square inch of ground surface, it does not seem unreasonable that plant life could have brought about this final result, given hundreds of millions of years in which to do it. Carbon, from which the oxygen of our atmosphere was separated, is now present in the earth's crust as graphite, coal, lignite, oil, hydrocarbon gases, and other carbonaceous materials.

Air-conditioning. For human comfort it is desirable to regulate the air in closed spaces, as in homes, places of business, and railway coaches, in respect to moisture and temperature. When air has taken up all the water vapor it can while in contact with water and at a given temperature, it is said to be saturated with water vapor. Sometimes this is expressed by saying that the *humidity* is 100 per cent. For comfort, the air should have a humidity of about 50 at the temperature of from 68° to 70° F.

By passing the air that is to be delivered to a room through a suitable absorbent of moisture, and at the same time regulating the temperature (see mechanical refrigeration), it is possible to bring the air of a room within these desirable ranges of humidity and temperature. This process is called *air-conditioning*. In warm weather, however, it is not desirable to reduce the temperature more than 10° below that of out-of-door air, for there is too much shock in suddenly passing from one temperature to the other. A simple air-conditioning apparatus is shown in Fig. 116.

Questions

1. How do you account for the fact that the rare elements in the atmosphere escaped detection until recent years?
2. Helium is approximately twice as heavy as hydrogen; yet a balloon (if we ignore its weight) filled with helium has more than 92 per cent of the lifting power of the same balloon filled with hydrogen. Explain.

3. What are some of the uses of the spectroscope in science and industry?
4. What properties must an element have to be useful in preparing nitrogen from the air?
5. There is four times as much nitrogen as oxygen in the atmosphere. Why not represent this fact by assigning to air the formula N_4O ?
6. What are the changes which may take place between the time when carbon dioxide is removed from the air by living organisms and the time when carbon dioxide is again returned to the air?
7. Why not use oxygen in place of carbon dioxide in the manufacture of soda water?
8. Suppose you had each of the gases so far studied in a separate cylinder and put a burning splint in each of the cylinders. What would happen in each case?
9. It is claimed by some scientists that, eventually, airplanes in traveling long distances will fly approximately 10 miles above the earth so as to be beyond the region of storms. What steps would have to be taken in order to make life possible at such a height?
10. In the modern developments to render the home more comfortable one plan contemplates an air-conditioning which involves increasing the humidity in winter and decreasing it in summer. Explain how such a scheme would serve a useful purpose.

Problems

1. The percentage by weight of moisture in a sample of air was determined by passing the air through a tube filled with calcium chloride (which removed all the moisture). Calculate the percentage from the following data:

Weight of air passed through the tube	16.2331 g
Weight of tube and contents (calcium chloride) at beginning of experiment	33.4652 g
Weight of tube and contents at end of experiment	33.6532 g

2. Twenty liters of air measured at 16° and 740 mm pressure was passed through two tubes: the first contained calcium chloride to remove the moisture, and the second a solution of sodium hydroxide to remove the carbon dioxide. Calculate from the following data the number of volumes of carbon dioxide present in 10,000 volumes of the air:

Weight of tube and contents (sodium hydroxide) at beginning of experiment	28.1323 g
Weight of tube and contents at end of experiment	28.1451 g

3. Suppose that 100 l of dry air (standard conditions) were passed over hot copper. (a) What weight of copper would be required to combine with the oxygen present? (b) What would be the volume of the residual gas? (c) What would be its composition?
4. Suppose you prepared nitrogen, using 100 g of sodium nitrite. (a) What weight of ammonium chloride would be required? (b) What volume of nitrogen (standard conditions) would be liberated? (c) What residue would be left in the flask in which the compounds were heated?
5. Suppose you wished to prepare 1000 l (standard conditions) of carbon dioxide by the action of hydrogen chloride (HCl) on pure marble. What weights (a) of hydrogen chloride and (b) of marble would be required?
6. What weight of carbon dioxide passed into a solution of calcium hydroxide would be required to form 20 g of calcium carbonate?

Reading References

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- MARTIN. "Solid Carbon Dioxide from Mexico," *Industrial and Engineering Chemistry*, Vol. XXIII, pp. 256-258.
- METZGER. "Traces from Tons," *Industrial and Engineering Chemistry*, Vol. XXVII, pp. 110-116. The article tells of the methods of recovering the rare gases from air.
- QUINN. *Journal of Chemical Education*, Vol. VII, contains three articles on the properties, uses, and commercial production of carbon dioxide, pp. 151-162, 403-419, and 637-652.
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CHAPTER 10

Water; Hydrogen Peroxide

WATER

Introduction. In contrast to the atmosphere, which is made up, for the most part, of a number of elementary gases, the hydrosphere is composed very largely of a single compound, water, and certain kinds of materials dissolved in it. Water is almost universal in its occurrence on our planet. It is present as ice and snow, as rain, as lakes and rivers, as a vapor in air, as underground waters, as an essential part of the soil, and as a constituent of many minerals. Vast areas of the colder regions of the globe are covered with ice. If the waters of the oceans, covering nearly five sevenths of the earth's surface, were spread out in a uniform layer over a sphere of the radius of the earth, the depth would be about 10,000 ft.

Properties. At ordinary temperatures pure water is a clear, transparent liquid. It has a slightly bluish color, but this is only noticeable in water of considerable depth, especially in lakes in which the water is fairly pure. It solidifies at 0° and boils at 100° under the normal pressure of the atmosphere at sea level. At higher elevations the pressure is less and the boiling point correspondingly lower. Thus, at Mexico City (elevation 7000 ft) water boils at 93° , while on the top of Mt. Everest (elevation 29,000 ft) it would boil at 71° . The density of water varies with its temperature, reaching its maximum at 4° , as shown in the following table:

TEMPERATURE	DENSITY	TEMPERATURE	DENSITY
0°	0.9998	40°	0.9923
4°	1.0000	60°	0.9833
10°	0.9997	80°	0.9719
20°	0.9982	100°	0.9586

A greater variety of matter is dissolved by water than by any other known solvent. Many substances, such as glass and various kinds of rock, which are ordinarily considered insoluble in water, really dissolve to a very limited extent. When perfectly pure, water is an almost complete nonconductor of the electric current; and compared

with other substances, a greater amount of heat is required to raise the temperature of a definite weight of it 1 degree.

The composition of natural waters. All natural waters contain small amounts of mineral matter, either in solution or held in suspension. Even the water which falls to the earth in the form of rain contains particles of dust, as well as small quantities of gases absorbed from the atmosphere. Upon reaching the earth's surface it dissolves mineral matter present in the rocks and soil, such as common salt and compounds of calcium, magnesium, and iron. Waters containing such substances in solution are commonly spoken of as *hard waters* or, if large amounts of mineral matter are present, as *mineral waters*. The quantity and nature of the substances present vary with the nature of the rocks and soil with which the water comes in contact. The weight of such matter present in 1 l of average well water varies from 0.1 to 0.5 g. Much larger quantities are present in the waters from some springs and very deep wells. The water of the ocean contains over 3.5 per cent of mineral matter, more than three fourths of which is common salt.

Salts in Average Dry Residue from Evaporated Sea Water

COMPOUND	FORMULA	AVERAGE PERCENTAGE
Sodium chloride	NaCl	77.76
Magnesium chloride	MgCl ₂	10.88
Magnesium sulfate	MgSO ₄	4.74
Calcium sulfate	CaSO ₄	3.60
Potassium sulfate	K ₂ SO ₄	2.46
Magnesium bromide	MgBr ₂	0.22
Calcium carbonate	CaCO ₃	0.34
		100.00

The water of the Great Salt Lake in Utah contains 23 per cent of solids, and that of the Dead Sea rather more. Large quantities of sodium chloride, bromine, and other useful substances are obtained by processing the water from oceans, salt lakes, and underground brines.

In addition to mineral substances natural waters contain more or less organic matter. This consists not only of inanimate matter, derived from the decay of organic substances on the earth's surface or present in sewage, but also of certain forms of living microorganisms (bacteria) which usually accompany such products. Waters taken from shallow wells or streams in thickly populated districts are likely to contain considerable quantities of such matter.

Pure water for chemical uses. For many purposes, and especially for laboratory uses, it is necessary to have pure water. This is obtained by removing the foreign matter from natural waters by the process of *distillation* (Fig. 117). With rare exceptions the foreign matter in natural water is nonvolatile; hence, if such water is boiled

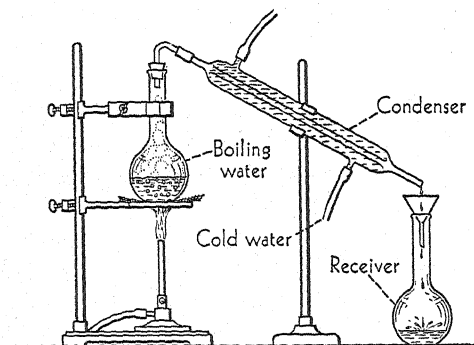


FIG. 117. Laboratory Distillation of Water

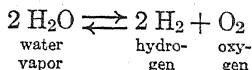
in a suitable vessel, the water passes off in the form of steam and may be condensed, while the impurities remain in the vessel. Water purified in this way is called *distilled water* and is sufficiently pure for nearly all purposes.

Chemical conduct. A knowledge of the chemical conduct of water is of fundamental importance for an understanding of many chemical processes. The main topics to be considered under this head are the effect of heat upon water, the reaction between water and certain elements and compounds, and the part that water plays in promoting chemical changes.

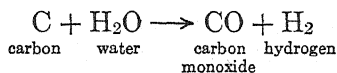
1. *The effect of heat upon water.* We have seen that in the formation of water from hydrogen and oxygen a great deal of heat is liberated (p. 110). The law of conservation of energy tells us that an equal amount of energy in some form will be required to decompose water. This may be supplied by the electric current, which, as we have seen, will effect the electrolysis of water. Heat alone will decompose it, although only to a slight extent even at very high temperatures. Compounds which are not readily decomposed by heat, such as water, are called *stable compounds*. The following table by Langmuir gives the percentages of the total quantity of water decomposed when heated in a closed system to the temperatures indicated. The results must be considered as approximate only, since the experiments are very difficult to carry out.

TEMPERATURE	PERCENTAGE OF WATER DECOMPOSED	TEMPERATURE	PERCENTAGE OF WATER DECOMPOSED
1327°	0.0446	1727°	0.504
1427°	0.0920	1927°	1.21
1527°	0.17	2227°	3.38
1627°	0.302	2728°	11.10

The decomposition of water by heat. When water is heated in a closed vessel to a temperature above the point at which perceptible decomposition begins, the percentage of the total vapor decomposed gradually increases with the rise in temperature. If, however, the temperature is maintained constant at any point, the decomposition *apparently* ceases. In reality it continues, but the oxygen and hydrogen formed combine again and at such a rate that the quantity of vapor decomposed in a given time is exactly equal to that formed by the union of the oxygen and hydrogen. In other words, the vapor is in equilibrium with its decomposition products, namely, oxygen and hydrogen. The change, therefore, like the change of oxygen into ozone, is a reversible one and may be expressed as follows:



2. The action of water as an oxidizing agent. Since water contains 88.81 per cent of oxygen, we might expect it to be a good oxidizing agent; but in general this is not the case. Stable bodies are not reactive, and the great stability of water prevents its parting with oxygen, save to powerful reducing agents. Some of the metals are oxidized by very hot steam, as we have seen to be true in the case of iron (p. 103). In a similar way red-hot carbon is oxidized by steam in the production of hydrogen by the Bosch process (p. 106):



3. The action of water upon oxides. Water combines with many of the oxides to form important compounds. It is convenient to divide these oxides into two general classes, according to the nature of the resulting compounds: (1) *acidic oxides*, which combine with water to form *acids*, and (2) *basic oxides*, which combine with water to form *bases*.

4. The action of water in the formation of hydrates. Many compounds other than oxides, especially those called salts, combine with water to form definite compounds when crystallized from solution. For example, the calcium chloride used in drying gases (Fig. 69) has the formula CaCl_2 . When crystallized from water, each molecule of this compound combines with 6 molecules of water to form a compound whose composition is expressed by the formula $\text{CaCl}_2 \cdot 6 \text{H}_2\text{O}$. The period between the two simple formulas signifies that the two kinds of molecules are chemically combined in the stated ratio. The crystals of blue vitriol, or bluestone, are composed of copper sulfate (CuSO_4) combined with water in the

ratio of 1 molecule of the sulfate to 5 of water, and the formula is $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$. When crystals such as these are heated, the water is driven off, but is regained when the salts are again crystallized from water solution.

The compounds before recombining with the water are called *anhydrous* substances, while the compounds formed by their union with water are called *hydrates*. Thus, blue vitriol is a *hydrate* of copper sulfate, while the white residue formed on heating this hydrate is *anhydrous* copper sulfate. Many anhydrous substances, however, form two or more different hydrates by combining with different percentages of water. The water which combines with compounds to form hydrates is termed *water of hydration*, or sometimes *water of crystallization*, because many hydrates are crystalline in character and, when heated, lose water, with an accompanying loss of their original crystalline structure. Compounds crystallized from water are usually hydrated.

It should not be inferred that all crystalline substances contain water of crystallization. The majority of minerals, such as quartz and diamond, are crystalline without having water of crystallization. Likewise some salts, such as sodium chloride, at room temperature crystallize from water in the anhydrous form.

5. The action of water in promoting chemical changes. Many substances which have no action upon each other in the absence of water readily enter into combination in its presence. The reason for this is not always clear. In some cases the increased activity seems to be due entirely to the fact that when in solution the substances are brought into more intimate contact. On the other hand, all electrovalent compounds dissolved in water exist wholly or in part as free ions (p. 40), and owe their great activity to these ions. Moisture also has a definite *catalytic* effect. Even a trace of water often has a marked influence in increasing the speed of certain chemical changes.

Methods for finding the exact composition of water. Many very careful experiments have been made for the purpose of determining, with as great accuracy as possible, the ratio in which hydrogen and oxygen are present in water; and it is worth our while to study somewhat in detail the methods which have been employed, since they illustrate in a striking way the types of procedure that are used in determining the composition of all compounds.

Two general methods are available for such a purpose: first, the *method of analysis*, in which a given weight of the compound is sepa-

rated either directly or indirectly into its constituent elements and the identity and weight of each determined; second, *the method of synthesis*, which consists in finding the proportion in which the constituent elements unite to form the compound, and which is therefore just the reverse of analysis.

Composition of water by analysis. It will be recalled that water may be decomposed easily into its constituents by the electric current. It would be expected that the exact composition of water could easily be found in this way, since the volumes of the gases liberated can be measured with accuracy; and, if we know their densities, the weights of the gases can be calculated. When the experiment is carried out, however, the results obtained are not concordant; in general, the volume of the hydrogen liberated is slightly more than double the volume of the oxygen. Experiments prove that the method is subject to several sources of error. For example, a portion of the oxygen liberated is converted into ozone; and the water through which the liberated gases bubble (Fig. 57, p. 88) dissolves more oxygen than hydrogen. The ratio between the weights of hydrogen and oxygen obtained in this process, therefore, does not represent with great accuracy the ratio in which they are combined in water. More accurate results are obtained by a number of synthetic methods, such as the ones now to be described.

Composition of water by synthesis. In the synthetic methods we measure directly the quantities of oxygen and hydrogen which combine to form water; or we may determine the quantity of either of the elements which enters into the combination and then the weight of the resulting water. The difference between these two weights is equal to the weight of the other element.

Eudiometer method of synthesis. A picture of the so-called *eudiometer tube*, used to measure the ratio of the volumes of gases which combine with one another, is shown in Fig. 118. The U-shaped tube is first filled completely with mercury. Pure hydrogen gas is introduced, through the stopcock into the graduated tube A, until it is about one-fourth filled, and the stopcock is then closed. While admitting the hydrogen, mercury is allowed to run out of stopcock C until it stands at exactly the same level in both arms of the U tube A and B. The gas enclosed in A is then at atmospheric pressure (since B is open to the atmosphere). The reading of the volume of hydrogen is taken. An approximately equal volume of pure oxygen is then introduced, the pressure is adjusted, and the volume again noted. This gives the total volume of the two gases. From this the volume of the oxygen may be determined by subtraction. The combination of the two gases is now brought about by connecting the two platinum wires with an induction coil and passing a spark through the mixture. Immediately a

slight explosion occurs. The mercury in the tube *A* is at first depressed because of the expansion of the gases by the heat generated in the reaction; but it at once rebounds, taking the place of the gases which have combined to form water. The volume of the water in the liquid state is so small that it may be disregarded in the calculations. In order that the temperature of the residual gas and of the mercury may become uniform, the apparatus is allowed to stand for a few minutes. After adjusting the pressure, by pouring mercury into *B*, the volume of the gas is read off and compared with the volumes of the hydrogen and oxygen originally taken. The residual gas is then tested to ascertain whether it is hydrogen or oxygen, for experiments have proved that it is never a mixture of the two. From the information thus obtained the composition of water may be calculated. For example, an experiment gives the following readings:

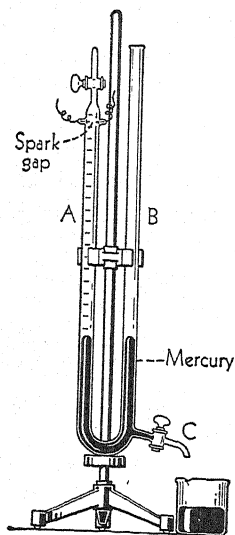


FIG. 118. A Simple Form of Eudiometer

Volume of hydrogen taken . . .	20.3 cc
Volume of hydrogen and oxygen	38.7 cc
Volume of oxygen	18.4 cc
Volume of gas left after combination has taken place (oxygen) . . .	8.3 cc

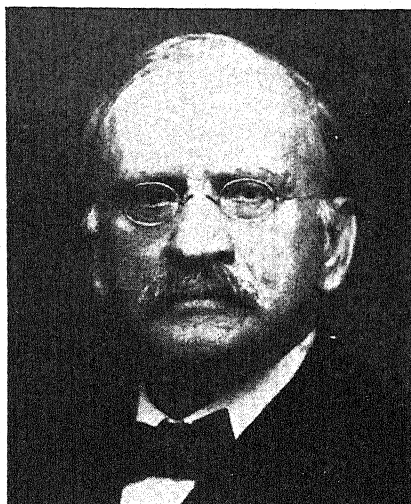
The 20.3 cc of hydrogen has combined with 18.4 cc minus 8.3 cc (or 10.1 cc) of oxygen, or approximately 2 volumes of hydrogen have combined with 1 volume of oxygen. Since oxygen is 15.90 times as heavy as hydrogen, the proportion by weight in which the gases combined is 1 part of hydrogen to 7.94 parts of oxygen.

The relation between a volume of aqueous vapor and the volumes of the hydrogen and oxygen which combine to form it. If the tube *A* of the eudiometer (Fig. 118) is jacketed with a larger glass tube, and is heated a little above 100° by allowing the vapor of a suitable boiling liquid to pass through the jacket, the water formed as a result of the union of the hydrogen and oxygen will not condense. Thus the volume of the water vapor may be measured. In this way it has been proved that 2 volumes of hydrogen and 1 volume of oxygen combine to form 2 volumes of water vapor, the volumes all being measured under the same conditions of temperature and pressure. It will be noted that the relation between these three volumes may be expressed by integer numbers.

Synthesis of water by Morley. The method used by Morley (Fig. 119) consists in weighing pure hydrogen and oxygen, as well as the water resulting from their combination.

As the average of twelve experiments Morley found that the proportion in which hydrogen and oxygen unite to form water is as follows: by weight, 1 part of hydrogen to 7.94 parts of oxygen; by volume, 2.0024 parts of hydrogen to 1 part of oxygen.

Experimental details. Fig. 120 represents the form of apparatus used by Morley for effecting the combination of hydrogen and oxygen and for weighing the resulting water. Extraordinary precautions were taken to insure pure materials and to eliminate all known sources of error. The air was first removed from the apparatus, which was then sealed and weighed. A tube containing hydrogen absorbed in palladium (the hydrogen is released on heating) was weighed and joined to the apparatus at *A*, while a large globe filled with oxygen was weighed and connected at *B*. The two gases were then admitted to the apparatus through the tubes *C*, *C*, and their union effected as they entered by electric sparks passed between the points at *D*. In order that the resulting steam might be condensed as fast as formed, the apparatus was immersed in cold water during the experiment. After from 30 to 35 g of water had been formed in this manner, the vessels from which the hydrogen and oxygen were supplied were disconnected and again weighed to determine the exact weights of hydrogen and oxygen admitted to the apparatus. There still remained in the apparatus, however, a certain amount of uncombined hydrogen and oxygen which had to be measured. To do this the entire apparatus was immersed in a freezing mixture until the water which had been formed by the union of the hydrogen and oxygen was frozen. The mixture of the uncombined gases was then withdrawn through *A* and *B*. Any moisture present in the mixture was removed as the gas passed through the tubes, *E*, *E*, which were filled with phosphorus pentoxide, a substance which has a strong affinity for water. The weights of hydrogen and oxygen present in the mixture were



Science Service

FIG. 119. *Edward Williams Morley*
(1838-1923)

From 1869 to his retirement in 1906, professor of chemistry in Western Reserve University. Known for his accurate determination of the densities of hydrogen and oxygen, and of the ratio in which they combine to form water; associated with A. A. Michelson in his classical researches on the relative motion of ether and matter and the determination of the length of the meter in terms of wave length of light; president of the American Association for the Advancement of Science (1895) and of the American Chemical Society (1899); recipient of many honors

then found by analysis. Finally the apparatus itself was weighed to measure the increase in weight due to the water formed in the experiment.

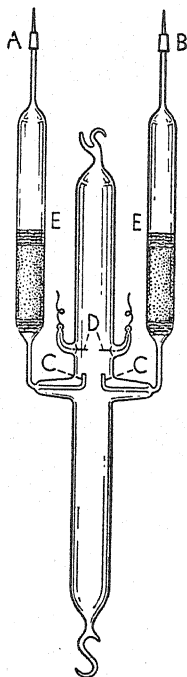


FIG. 120. Diagram of Apparatus Used by Morley for the Quantitative Synthesis of Water

Comparison of results obtained. From the description of these methods it is easy to see that experiment alone can determine the composition of a compound. Different methods will sometimes lead to slightly different values. The more reliable the method chosen, and the greater the skill with which the experiment is carried out, the more accurate will be the results. It is universally conceded that Morley's results are the most trustworthy yet obtained.

The formula for water. If we should wish to translate the ratio in which hydrogen and oxygen enter into the composition of water (1 g hydrogen: 7.94 g oxygen) into the *percentage composition* of water, we should calculate as follows: $\frac{1}{8.94} \times 100$, or 11.19 per cent hydrogen, and $\frac{7.94}{8.94} \times 100$, or 88.81 per cent oxygen. Since the molecular weight of water is approximately 18 (Dumas method, p. 78), we conclude that a gram-molecular weight of water contains

18 \times 0.8881 = 15.986 g oxygen
and 18 \times 0.1119 = 2.014 g hydrogen

Inasmuch as a molecule of a compound consists of a *definite whole number* of atoms of its constituent elements, it follows that a gram-molecular weight of the compound consists of the same *definite whole number* of gram-atomic weights of the constituent elements. To find the formula for water, then, we must find how many gram-atomic weights of oxygen are represented by 15.986 g, and how many gram-atomic weights of hydrogen correspond to 2.014 g. We can obtain the desired numbers by dividing these weights, respectively, by the atomic weights of oxygen and hydrogen:

$$\frac{15.986}{16} = 0.999, \text{ or approximately 1 g-at. wt of oxygen}$$

$$\frac{2.014}{1.008} = 1.999, \text{ or approximately 2 g-at. wt of hydrogen}$$

Recognizing that the values for molecular weights cannot be measured with as great an accuracy as atomic weights and combining ratios, we accept the whole numbers nearest to the values obtained in our calculation and conclude that *one* gram-molecular weight of water contains *one* gram-atomic weight of oxygen and two gram-atomic weights of hydrogen. So the formula for water is H_2O . The formulas for other compounds may be found in exactly the same way.

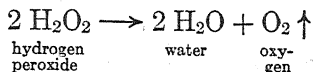
HYDROGEN PEROXIDE

Composition. In 1818, while studying the action of acids upon certain oxides, the French chemist Thenard discovered the compound which we now call *hydrogen peroxide*, or sometimes *hydrogen dioxide*. The pure compound is a liquid and, like water, is composed of hydrogen and oxygen. The proportions in which the hydrogen and oxygen are present in these two compounds, however, are widely different, as follows:

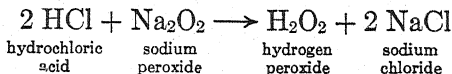
Water 1 part of hydrogen to 7.94 parts of oxygen by weight
 Hydrogen peroxide. . . . 1 part of hydrogen to 15.88 parts of oxygen by weight

In other words, *the weight of oxygen combined with a fixed weight of hydrogen is just twice as great in hydrogen peroxide as in water.* Since the formula for water is H_2O , the formula for hydrogen peroxide must be HO or some multiple of HO . Experiments show that the peroxide has a molecular weight of approximately 34; hence its formula must be H_2O_2 . This large percentage of oxygen is indicated by the name *peroxide*, the prefix *per* meaning "more" or "excess."

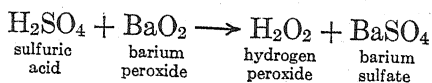
Preparation. While a dilute solution of hydrogen peroxide in water may easily be obtained, the pure compound cannot be prepared without great difficulty, since it decomposes readily into water and oxygen, thus:



Dilute solutions of the compound are prepared by the action of acids on peroxides of the metals, the process being conducted at a low temperature so as to prevent the decomposition of the hydrogen peroxide. For laboratory purposes one can readily obtain it along with sodium chloride in solution, by the action of hydrochloric acid on sodium peroxide:



Commercially it is prepared (1) by electrolysis of dilute solutions of sulfuric acid or ammonium sulfate or (2) by the action of acids on barium peroxide that has been hydrated with steam :



Properties. Hydrogen peroxide is a sirupy liquid, colorless unless seen through thick layers of the liquid, when it has a slightly bluish tint. Its density is 1.442 and its boiling point 152.1°. Its decomposition into water and oxygen is attended by the evolution of heat amounting to 676 cal for each gram decomposed.

Since hydrogen peroxide so readily decomposes, with evolution of oxygen, it acts as a strong oxidizing agent even in very dilute solutions. An easily oxidizable substance, like wool, is ignited by the addition of a few drops of the pure compound. The speed of decomposition of hydrogen peroxide is modified by many conditions. In dilute solutions and at a low temperature the speed is very slow, while at higher temperatures and in more concentrated solutions it becomes so great as to cause violent explosions. Moreover, it is greatly affected by the presence of certain catalysts (p. 89). Thus, a little finely divided platinum or manganese dioxide, added to a solution of the peroxide, greatly accelerates the evolution of oxygen gas. Certain organic substances, including those present in blood, have a similar action. Other substances have the opposite effect and retard the decomposition. Catalysts that retard the speed of a reaction are known as *negative* catalysts to distinguish them from *positive* catalysts, which increase the speed of a reaction. The commercial solution of hydrogen peroxide contains a small amount of a negative catalyst to preserve its strength — usually a trace of acid or some organic compound (often acetanilide).

Uses. Hydrogen peroxide has many commercial uses, all based on its strong oxidizing properties. The common medicinal peroxide of the druggist is an aqueous solution containing 3 per cent by weight of the compound. This solution has been largely used as a germicide, but experiments indicate that it is not very effective for this purpose. Like ozone, it acts upon certain dyes and natural colors, such as that of the hair, oxidizing them into colorless compounds; consequently it is sometimes used as a bleaching agent. The chemist finds it especially useful as an oxidizing agent in many analytical operations. A 30 per cent solution, known as *perhydrol*, is now commercially available for chemical uses.

Questions

1. What is a method for determining (a) the percentage of solids in a sample of water; (b) the percentage of water in a sample of milk?
2. Suppose that water, like most other liquids, continued to increase in density with the lowering of the temperature, even when frozen into ice. What would be some of the natural results that would be (a) to our advantage; (b) to our disadvantage?
3. What are the differences between the following terms: *hydride*, *hydrate*, and *anhydrous*?
4. There are a great many colorless liquids. How can you tell if any one of such a group is water?
5. When sugar is heated, water is evolved. (a) Does this prove that sugar contains water? (b) What does it prove?
6. In determining the composition of water by the union of hydrogen and oxygen (Fig. 118), an excess of one of the gases is always used. Why?
7. (a) What are the different methods employed in determining the composition of a compound? (b) The results obtained by different investigators are rarely identical. Why not? (c) If the results differ, which should be accepted?
8. In order to calculate the formula of a compound, what information must one have?

Problems

1. A sample of milk was poured into an evaporating dish, and the dish and contents were heated to 100° , until there was no further loss in weight. From the following data calculate the percentages (a) of water and (b) of solid matter in the milk:

Weight of dish	22.1823 g
Weight of dish and milk	31.1614 g
Weight of dish and contents after heating	23.5301 g

2. The ratio in which hydrogen and oxygen combine was determined by introducing known volumes of hydrogen and oxygen into a eudiometer (Fig. 118) and then, with an electric spark, bringing about their combination. Calculate, from the following data, the ratio (a) by volume and (b) by weight in which the two gases combine, assuming all measurements to be made under standard conditions:

Volume of hydrogen	12.3 cc
Volume of hydrogen and oxygen	25.4 cc
Volume of gas (oxygen) left after combination has taken place	6.95 cc

3. Calculate from the following data the percentage of oxygen in a sample of dry air:

Volume of air in tube (Fig. 118)	32.00 cc
Volume after introducing an excess of hydrogen	52.50 cc
Volume after passing a spark through the mixture	31.84 cc

4. Morley found the composition of water by determining the weights of hydrogen and oxygen that combine with each other to form water. The results of four trials were as follows:

HYDROGEN USED	OXYGEN USED	HYDROGEN USED	OXYGEN USED
(1) 3.2645 g	25.9176 g	(3) 3.8193 g	30.3210 g
(2) 3.2559 g	25.8531 g	(4) 3.8450 g	30.5294 g

In each case calculate the ratio in which the hydrogen and oxygen combined to form water.

5. Suppose you had 100 g of barium peroxide. (a) What weight of the hydrogen peroxide of the druggist could you prepare from it, assuming no hydrogen peroxide to be lost? (b) What weight of sulfuric acid (H_2SO_4) would be required in the preparation?

6. The gas known as *phosgene*, used largely as a poisonous gas in war, has the following composition: carbon, 12.13 per cent; oxygen, 16.17 per cent; chlorine, 71.69 per cent. Its molecular weight is approximately 100. Calculate its formula.

7. A certain gaseous compound has the following composition: nitrogen, 82.24 per cent; hydrogen, 17.75 per cent. Two hundred cubic centimeters of the compound weighs 0.1542 g. Calculate its formula.

8. What volume of oxygen, measured under standard conditions, may be obtained by the catalytic decomposition of the hydrogen peroxide in 500 g of the ordinary solution sold by a druggist?

Reading References

- CLARKE. *Marvels of Modern Chemistry*. Chapter XII deals with water.
 FOSTER. *The Romance of Chemistry*. Pages 99–110 tell of water and hydrogen peroxide.
 REINMUTH. "Water and Its Components," *Journal of Chemical Education*, Vol. V, pp. 1163–1167.

CHAPTER 11

Oxides and the Earth's Crust

Importance of the oxides. The most abundant of all compounds in the crust of the earth are the oxides (chiefly the complex oxides which simple oxides form with one another). It is very important that we describe the general nature of oxides and their behavior in various types of chemical reactions. Chemists have known and studied some of the oxides for a long time, and these compounds have played a most significant role in the development of the science of chemistry.

Chemical structure of the earth. In Chapter 9 we have already calculated the total weight of the atmosphere from the pressure of the atmosphere per unit area, and from the total area of the earth's surface. Let us now again make use of the size of the earth to show some of the interesting things about the arrangement and distribution of different kinds of matter within the earth. Since the radius of the earth is about 6.37×10^8 cm, its volume ($\frac{4}{3} \pi r^3$) is about 1.083×10^{27} cc. If the earth-sphere were wholly water (density = 1), the weight would therefore be about 1.083×10^{27} g. Actually the weight of the earth is about 5.98×10^{27} g. The *average* density of the earth may be calculated by dividing its weight by its volume, and is about 5.52. ($5.98 \times 10^{27} \div 1.083 \times 10^{27} = 5.52$.)

But the density of the rocks in the earth's crust is about 2.8, and consequently we must infer that the earth's interior is made up of materials much more dense than those in the crust. Much of our inference about the internal structure is based on a study of the velocity of earthquake waves which reach the various seismograph stations located around the earth. A wave may start, say, at a point *A* (in Fig. 121) and travel through the crust and also through the interior at different depths to points *B*, *C*, and *D*. Since the velocity depends on the density of the medium through which the waves travel, we have here the basis for an estimate of density at various depths. The best present theory of the nature of the earth's interior is illustrated in Fig. 121. A central core about 3400 km (2100 miles) in radius is thought to be made up of iron (and nickel) and to have a density of approximately 10. Whether it is liquid or solid is not known. Around this core there is a transition layer, of the thickness shown in the figure, and then there is a magnesium-iron silicate

layer of density approximately 4. On top of all is the crust (lithosphere) of the earth, 60–100 km deep (36–60 miles).

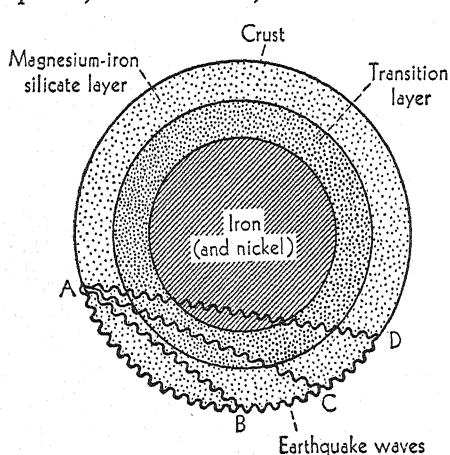


FIG. 121. *Diagram of Supposed Composition of the Earth*

Abundance of elements in the earth's crust. Man has not yet been able to drill wells or dig mines much deeper than 2 miles; but geologists have obtained a good idea, from the faulting and uplifting of strata and enormous masses of rock, of what the crust is like down to depths of perhaps 10 miles. Systematic sampling and chemical analysis have been made for many years in the effort to learn the distribution and abundance of the various elements. The following table shows the average composition

of the 10-mile-deep earth's crust in terms of the most commonly found elements:

Elements in the Earth's Crust (Exclusive of the Oceans and Atmosphere)

ELEMENT	PER CENT	ELEMENT	PER CENT
Oxygen	46.71	Magnesium	2.08
Silicon	27.69	Titanium	0.62
Aluminum	8.07	Hydrogen	0.14
Iron	5.05	Phosphorus	0.13
Calcium	3.65	Carbon	0.094
Sodium	2.75	Other elements	0.436
Potassium	2.58		100.000

Oxygen constitutes almost half of the total; silicon more than a quarter; the first five elements, oxygen, silicon, aluminum, iron, and calcium, more than 91 per cent; and the twelve elements listed above, more than 99.5 per cent. Some of the other elements are extremely rare and difficult to find.

What may have happened when the earth cooled. Let us suppose that all the earth was at one time a hot glowing mass of vapor which gradually cooled, by radiation of its heat, and condensed to liquid

and finally largely to solid. As the mass cooled to sufficiently low temperatures, oxides were formed. It is likely that iron made up a very considerable portion of the original mass, but that the oxides of iron (and nickel) were not formed until relatively low temperatures were reached, late in the process of cooling. In the meantime, the vast masses of metallic iron (and nickel), being very dense, were largely segregated at the center. The much lighter oxides collected in regions outside of this core, and the lightest ones at the very top. Finally, at still lower temperatures, oxides combined chemically with other oxides to give complex oxides.

Oxides of metals and nonmetals. We have described, in Chapter 6, the formation of several oxides by the burning of elements in oxygen. All the elements, with the exception of the rare gases, form oxides. These oxides are divided into two great classes, of distinctively different properties and behaviors: the *oxides of metals*, such as those of iron, magnesium, and aluminum, and the *oxides of nonmetals*, such as those of carbon, phosphorus, and silicon. Some of the elements react vigorously with oxygen, even in air at room temperature (phosphorus, sodium); others react only when hot (hydrogen, silicon, carbon, iron). Some oxides can be prepared only by indirect methods.

The free, simple oxides which can be found as native minerals in the earth's crust today are very few indeed and are about as follows (with their mineralogical names): Al_2O_3 (corundum), SiO_2 (quartz), Fe_2O_3 (hematite), TiO_2 (rutile), ZnO (zincite), Cu_2O (cuprite), and of course water itself (which is an oxide). But all the oxides can be prepared in the laboratory. In the table which follows there are listed some oxides of the most abundant elements in the earth's crust, as well as a few others of much interest:

METALLIC OXIDES			NONMETALLIC OXIDES		
ELEMENT	OXIDE	STATE	ELEMENT	OXIDE	STATE
Al	Al_2O_3 , aluminum oxide	solid	Si	SiO_2 , silicon dioxide	solid
Fe	FeO , ferrous oxide	solid	Ti	TiO_2 , titanium oxide	solid
	Fe_2O_3 , ferric oxide	solid	P	P_4O_{10} , phosphorus pentoxide	solid
Ca	CaO , calcium oxide	solid	C	CO_2 , carbon dioxide	gas
Na	Na_2O , sodium oxide	solid	S	SO_2 , sulfur dioxide	gas
K	K_2O , potassium oxide	solid		SO_3 , sulfur trioxide	liquid
Zn	ZnO , zinc oxide	solid	N	N_2O_5 , nitrogen pentoxide	solid
Ag	Ag_2O , silver oxide	solid			

The structure of the oxides of metals. Nearly all the oxides of metals are solid (at ordinary temperatures); they are all *electrovalent* compounds; their crystal lattices are built of *ions*. X-ray analysis clearly shows that calcium oxide (lime) has its ions arranged as indicated in Fig. 122. This is the same pattern as that of the sodium chloride lattice (p. 134). The only difference, aside from the size of the ions, is that here the ions carry *two* charges, Ca^{++} and O^{--} , whereas the ions of sodium and chlorine are singly charged. Magnesium oxide has the same structure as calcium oxide.

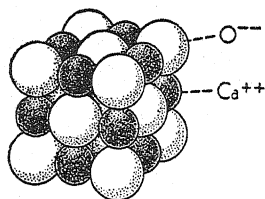


FIG. 122. *Crystal Lattice of Calcium Oxide*

We also show the lattice for silver oxide, Ag_2O , Fig. 123. All those metallic oxides which can be fused to a liquid without decomposition conduct the electric current.

The structure of the nonmetallic oxides. The *nonmetallic* oxides belong almost entirely to the *covalent* type of compounds; their atoms are not held together as ions, but are joined by covalent bonds (p. 38) in individual molecules. When the nonmetallic oxide is a solid, or is frozen to a solid, its crystal lattice is usually built up of separate molecules piled together in some characteristic ordered arrangement. In Fig. 124, which shows the lattice of carbon dioxide as an example, the individual molecules can be clearly recognized.

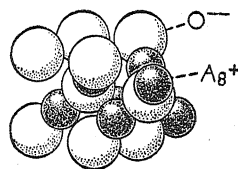


FIG. 123. *Crystal Lattice of Silver Oxide*

Deduction of the formula for a covalent compound. The formula for a covalent compound, water, has already been deduced (H_2O) in the preceding chapter. A general method for finding what the formula of any covalent compound is will now be presented. Four things must be known: (1) what elements are in the compound, (2) the atomic weights of these elements, (3) the approximate molecular weight of the compound, and (4) the percentage composition. Let us go through the procedure of deducing the formula for the compound carbon dioxide, to illustrate the reasoning involved.

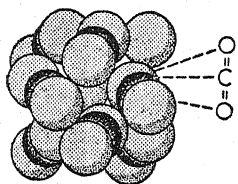


FIG. 124. *Crystal Lattice of Carbon Dioxide*

The formula for carbon dioxide. (1) It is known that *carbon* and *oxygen* are the elements present in this compound, because by starting with them, and with no other elements present, carbon dioxide can be prepared (by burning carbon in oxygen). (2) The atomic

weights are known to be 16.00 for oxygen (by definition) and 12.01 for carbon (positive-ray method). (3) The *approximate* molecular weight of the gas may be found by the Dumas method (p. 78), and a typical result is 45. (4) Finally, in the case of this particular compound, the percentage composition can be found experimentally as follows: A weighed quantity

of carbon, purified with great care, is placed in a small porcelain boat (Fig. 125) and is heated to redness. Pure oxygen gas passes over it, unites with it to form carbon dioxide, and sweeps this into the bubbler bulbs, where the carbon dioxide reacts with a strong solution of potassium hydroxide and is retained in the solution as potassium carbonate (K_2CO_3).

The increase in weight of the bubbler, therefore, is the weight of the carbon dioxide produced. In a typical synthesis of this sort, 0.0359 g carbon united with oxygen to give 0.1321 g carbon dioxide. Consequently the percentage of *carbon* in carbon dioxide is $\frac{0.0359}{0.1321} \times 100 = 27.2$ per cent; and the percentage of oxygen is 100 per cent - 27.2 per cent = 72.8 per cent.

Then, with all the information we need, we proceed with our deduction of the formula:

27.2 per cent of 45 g = 12.2 g (which is the *approximate* weight of *carbon* in 1 g-mol. wt of carbon dioxide)

72.8 per cent of 45 g = 32.8 g (which is the *approximate* weight of *oxygen* in 1 g-mol. wt of carbon dioxide)

Since the gram-atomic weights of carbon and oxygen are 12.01 g and 16.00 g, it follows that there are about $\frac{12.2}{12.01}$, or 1.02, g-at. wt of carbon, and about $\frac{32.8}{16}$, or 2.05, g-at. wt of oxygen in 1 g-mol. wt

of carbon dioxide. But *whole numbers* of gram-atomic weights of elements make up the gram-molecular weight of a compound; and our results would have shown exactly whole numbers except for small unavoidable experimental errors in finding the molecular weight. The formula for carbon dioxide must therefore be CO_2 , and

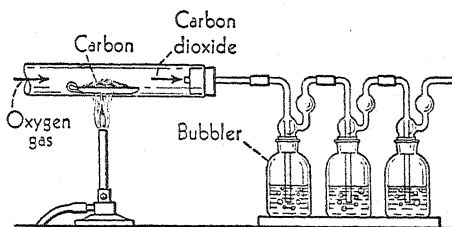


FIG. 125. Apparatus for Determining the Composition of Carbon Dioxide

the *exact* molecular weight 44.01. This formula agrees with the conclusion reached by X-ray analysis (Fig. 124).

Deduction of the formula for an electrovalent compound, silver oxide. By a method very much like the one followed with a covalent compound, the formula of an electrovalent compound may be found. Let us use the compound silver oxide as an illustration; but instead of building up the compound from its elements (*synthesis*), let us adopt the procedure of breaking it down into its elements (*analysis*).

Silver oxide (say 1.8541 g) decomposes completely, if heated in a crucible to a moderately high temperature, to give a metallic silver bead weighing 1.7271 g. The quantity of oxygen liberated can then be found by subtraction:

$$1.8541 \text{ g silver oxide} - 1.7271 \text{ g silver} = 0.1270 \text{ g oxygen}$$

The atomic weight of silver is known, 107.88 (p. 49); and of course the atomic weight of oxygen is 16.00. The "molecular weight" of an electrovalent compound means the weight of the *simplest set of ions* which will represent the ratio in which the ions occur in the whole crystal lattice.

This simplest set of ions for silver oxide can be deduced by finding the number of gram-atomic weights of oxygen combined with 1 g-at. wt of silver:

$$\frac{1.7271 \text{ (g silver left in crucible)}}{107.88 \text{ (g-at. wt of silver)}} = \frac{0.1270 \text{ (g oxygen liberated)}}{x}$$

On solving the proportion, x is found to be 7.93 g. This is close enough to 8.00 g to indicate that $\frac{1}{2}$ g-at. wt of oxygen is combined with 1 g-at. wt of silver, and to indicate that the formula might be $\text{AgO}_{\frac{1}{2}}$. But atoms and ions do not combine by halves, and we recognize that Ag_2O is the simplest set of atoms, or rather that $(2 \text{ Ag}^+, \text{O}^{--})$ is the simplest set of ions. This is the formula for silver oxide (checked by X-ray analysis). By similar procedures the formulas of all the metallic oxides have been deduced.

Valence. In Chapter 3 *valence* was briefly discussed. The metallic and nonmetallic oxides may now be used to illustrate more fully the meaning of this extremely important word in the chemist's vocabulary. Valence is a number. It is a property of an atom or of an ion. *The valence of an atom or ion is the number which tells how many atoms or ions of another kind a given atom or ion can hold in combination or can displace in a reaction.* Consequently, if the formula of a molecule is known, the valences of its atoms or ions can be told.

Valence in an electrovalent compound. In the simplest set of ions, which is the molecule of an electrovalent compound, the valence of the different ions is *the number of unit electric charges* carried by the ions. Ions of positive charge have a *positive valence*, and those of negative charge a *negative valence*. In the molecules of the metallic oxides ($2\text{Na}^+, \text{O}^{--}$), ($\text{Ca}^{++}, \text{O}^{--}$), ($2\text{Al}^{+++}, 3\text{O}^{--}$), the valence of the oxygen ion is 2, as always. The valence of Na^+ is 1, and the ion is called *univalent*; Ca^{++} has a valence of 2, and it, like O^{--} , is *bivalent*; Al^{+++} is *trivalent*; an ion carrying 4 charges, like Mn^{++++} in MnO_2 (manganese dioxide), is *quadrivalent*, as is also the complex ion SiO_4^{----} . A valence as high as 8 is known, but no higher. Sometimes a given atom shows more than one valence; that is, it forms different ions which carry different numbers of unit charge, like Fe^{++} and Fe^{+++} in FeO and Fe_2O_3 .

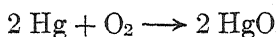
The molecule of an electrovalent compound is neutral and necessarily contains equal numbers of + and - charges. The hydrogen ion, H^+ , and the chlorine ion, Cl^- , each carry *one* charge, and so are used as *standards* for judging, from the number of H^+ displaced or of Cl^- electrically balanced by a single metallic ion, what the valence of that metallic ion is.

Valence in covalent compounds. Here the valence of an atom is *the number of covalent bonds* by which the atom is united to neighboring atoms in the same molecule. "Positive valence" and "negative valence" have no significant meaning in this case, because the molecule is not made up of positive and negative ions. It has already been stated (p. 43) that in the molecules $\text{H}-\text{Cl}$ (hydrogen chloride), $\text{H}-\text{O}-\text{H}$ (water), NH_3 (ammonia), CH_4 (methane), and PCl_3 (phosphorus trichloride), the atoms H and Cl have a valence of 1, O a valence of 2, N and P a valence of 3, and C a valence of 4. These conclusions have been reached from the formulas by using H and Cl (rather than H^+ and Cl^- , as in electrovalent compounds) as standards. Both these atoms, in covalent compounds, bind themselves to other atoms by *single* bonds, and they also unite with each other and with atoms of their own kind by single covalent bonds: $\text{H}-\text{Cl}$, $\text{H}-\text{H}$, $\text{Cl}-\text{Cl}$. So, to find the valence of any atom *A* toward H or Cl, that is, the number of bonds which atom *A* extends, we proceed to *find experimentally* how many gram-atomic weights (or gram-equivalent weights) of hydrogen or chlorine are combined with 1 g-at. wt of *A* in the compound in question.

Variable valence. While a nonmetallic atom generally shows some favorite valence which is the same in most of its compounds, when tested by the H-atom, Cl-atom, and O-atom standards its

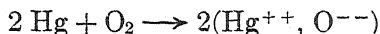
valence is *not always* constant. The atom of phosphorus shows a valence of 3 in P_4O_6 (phosphorus trioxide) and of 5 in P_4O_{10} (phosphorus pentoxide); also it forms PCl_3 and PCl_5 ; it forms PH_3 (phosphine) but not PH_5 . The sulfur atom gives SO_2 (sulfur dioxide), SO_3 (sulfur trioxide), and H_2S (hydrogen sulfide). Although carbon forms two oxides, CO (carbon monoxide) and CO_2 (carbon dioxide), it does not form CH_2 and CCl_2 but only CH_4 and CCl_4 .

Oxidation and reduction. The terms *oxidation* and *reduction* have been inherited by modern chemists from at least as far back as 1800. Lavoisier's early investigation of combustion showed that a metal — for example, mercury — combines with oxygen to form an oxide,



and it was only natural to call such a reaction, involving the addition of oxygen, an oxidation. In a similar way the removal of oxygen was defined as reduction. It was in this sense that oxidation and reduction were used in earlier chapters.

Oxidation and reduction in electrovalent compounds. Some thirty years ago, when we learned a little more about the nature of the reaction above and similar reactions, we began to write the equation for the action of mercury on oxygen thus:

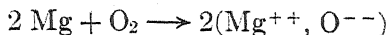


The important thing which happens in this act of combination is the acquisition of a positive charge by the metallic atoms and of a negative charge by the oxygen atoms. The two atoms in the oxygen molecule part, and each one accepts 2 electrons, given up, in this particular case, by each atom of mercury. The ions of the oxide are thereafter held together by electrostatic attractions in a crystal lattice. The same act of electron loss and gain may occur when other elements unite with a metal (iron reacts with chlorine, $2 \text{Fe} + 3 \text{Cl}_2 \longrightarrow 2(\text{Fe}^{+++}, 3 \text{Cl}^{-})$); and the original meaning of *oxidation* was gradually broadened to include all such cases, even when no oxygen was involved.

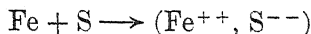
In its broad sense, *oxidation of an atom or ion is an increase in positive valence or a decrease in negative valence*; and *reduction*, which is just the reverse of oxidation, *is a decrease in positive valence or an increase in negative valence*. Oxidation and reduction always occur together and in equal amount. The substance that loses electrons is *oxidized* and is called a *reducing agent*, whereas the one that receives the electrons is *reduced* and is called an *oxidizing agent*.

Examples of oxidation and reduction in electrovalent compounds. We may now give a few typical examples of oxidation-reduction reactions in electrovalent compounds.

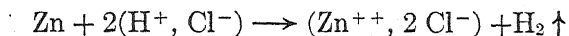
1. The reactions of all the metallic elements with oxygen to form oxides are oxidation-reduction reactions. The metal is oxidized, and the oxygen is reduced; for example,



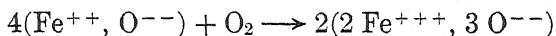
2. In the combination of iron and sulfur, the iron is oxidized and the sulfur reduced:



3. In the displacement of hydrogen from an acid by a metal, the metal is oxidized and the hydrogen reduced:

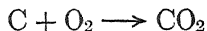


4. A metallic ion of a given positive valence may have its positive charge increased and so be oxidized:

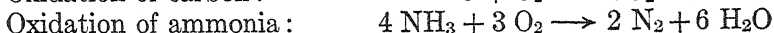


Oxidation and reduction in covalent compounds. The terms *oxidation* and *reduction* as applied to electrovalent compounds cannot be readily transferred to covalent compounds, because the latter do not carry electric charges. With covalent compounds we may best return to a modified statement of the original definition of oxidation and reduction, as follows: *Oxidation of a compound or element is the addition to it of oxygen or the removal of hydrogen. Reduction is the reverse process: the removal of oxygen or the addition of hydrogen.* The following equations illustrate these definitions:

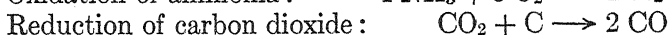
Oxidation of carbon:



Oxidation of ammonia:



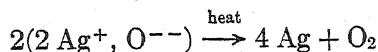
Reduction of carbon dioxide:



Reduction of carbon:



Decomposition of oxides by heat (thermal decomposition). In the analytical procedure followed for the deduction of the formula for silver oxide, a weighed quantity of the oxide was heated until it decomposed:



Other oxides can be split thermally in the same way, although the temperature must be extremely high in some cases.

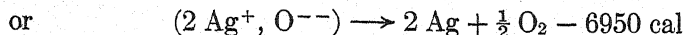
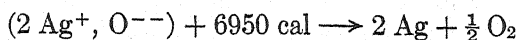
This decomposition reaction is an oxidation-reduction reaction, just the reverse of what would happen if silver were burned in oxygen. As indicated in the equation above, the oxygen ions, O^{--} , lose their 2 electrons (and are therefore *oxidized*), and the silver ions, Ag^+ , gain electrons (and are *reduced*). Neutral atoms of silver are formed, and the atoms of oxygen double up to form molecules of oxygen, O_2 .

Heat of decomposition. Any reaction, like the decomposition of silver oxide, which proceeds only when heat is *absorbed* is called an *endothermic* reaction (p. 95). The quantity of heat required will depend not only on the nature of the compound, but also on the quantity of the compound to be decomposed. The heat, expressed as calories, required to decompose *one gram-molecular weight* of a compound is called the *heat of decomposition*, or the *heat of the reaction*. For silver oxide, 231.76 g ($2 \times 107.88 + 16$), it is 6950 cal , which is an unusually small heat of decomposition. The heats of decomposition for several oxides are given in the table below.

SUBSTANCE	HEAT OF DECOMPOSITION	SUBSTANCE	HEAT OF DECOMPOSITION
ZnO	84,350 cal	Ag_2O	6,950 cal
MgO	145,800	SiO_2	198,300
FeO	64,000	SO_2	75,270
Al_2O_3	399,050	CO_2	94,385

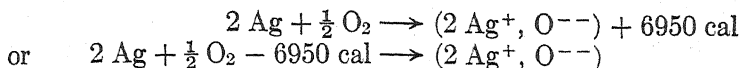
Heat of formation. Decomposition reactions nearly always absorb heat; and the reverse reactions, namely, *combination* reactions, nearly always give out heat, and are called *exothermic*. Thus, when silver reacts with oxygen to form silver oxide, heat is liberated; and for 1 g-mol. wt of silver oxide *formed*, the heat is exactly the same (6950 cal) as for 1 g-mol. wt of silver oxide decomposed. This statement holds for all chemical reactions, namely, that the heat absorbed when the reaction goes in one way is equal to the heat liberated when the reaction goes in the other way (law of conservation of energy).

Thermal equations. Often the heat of reaction is *indicated in the equation*, thus:



In these equations we start with *one* g-mol. wt of silver oxide and hence would have to show $\frac{1}{2}$ g-mol. wt of oxygen (the $\frac{1}{2} O_2$ is not intended to mean that a half-molecule is obtained).

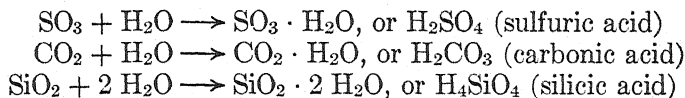
For the reverse reaction, in which the elements silver (in finely divided form) and oxygen (under pressure) unite to form the oxide, we would write the equation thus :



The reaction of metallic oxides and nonmetallic oxides with water. Of the several properties and behaviors which distinguish the two great classes of oxides from each other, the most striking is their reaction with water. A metallic oxide unites chemically with water to form a *base*, and a nonmetallic oxide unites with water to form an *acid*. Some of the oxides react with water vigorously, others very slowly. Some of the acids and bases thus produced are soluble in water; others are extremely insoluble.

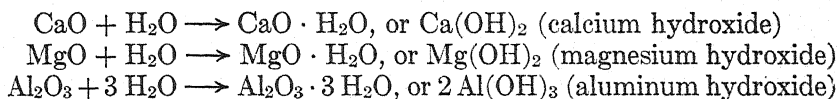
Equations for the reactions of some oxides with water to form acids and bases are as follows :

Acids :

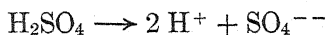


(Silicic acid forms and goes into solution readily only in superheated water.)

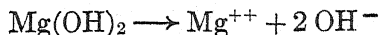
Bases :



The molecules of an acid are characterized by the presence of hydrogen atoms, as in sulfuric acid, H_2SO_4 . In water solution an acid molecule furnishes hydrogen ions, H^+ :

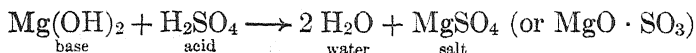
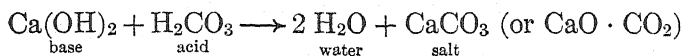


In much the same way the molecules of a base are characterized by the presence of hydroxyl groups, OH , as in $\text{Mg}(\text{OH})_2$; and in water solution a molecule of a base yields hydroxyl ions, OH^- :



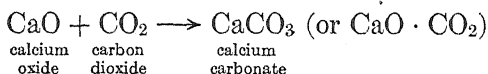
Action of an acid on a base. Since the action of oxides of metals on water results in the formation of compounds (bases) very different from those produced by the action of nonmetallic oxides on water (acids), it is of great interest to find how these hydrated oxides (acids and bases) act on each other. Experiment shows that

in general every acid acts with every base in a reaction that eliminates water and forms a type of compound called a *salt*, as illustrated in the equations



A much more extended description of acids, bases, and salts will be found in a later chapter.

The formation of salts directly from oxides. The question at once arises, Will metallic oxides react directly with nonmetallic oxides to form salts? Under proper conditions reactions of this kind take place easily. For example, if calcium oxide (lime) and the gas carbon dioxide are brought together, we get the *salt* calcium carbonate, CaCO_3 :



Reactions of this kind are more often brought about by *melting* the two oxides together, since most oxides are solids at ordinary temperatures. By this means we can get magnesium silicate, Mg_2SiO_4 :



A large variety of salts can be prepared by these fusion reactions, and many of them are identical with those prepared by the action of a base on an acid.

Complex oxides in nature. Near the beginning of this chapter we were describing what might have happened chemically while the earth was cooling, and we said, "As the mass cooled to sufficiently low temperatures, oxides were formed." We can now understand more fully the meaning of such a statement, since we know that at very high temperatures no oxides could exist, but would all be decomposed. The free, simple oxides which can be found as native minerals in the earth's crust today are not very many, as we have pointed out. However, *many* occur as constituents of complex oxides (salts) — for example, $\text{CaO} \cdot \text{CO}_2$ (calcite, limestone, marble), $\text{CaO} \cdot \text{SO}_3 \cdot 2 \text{ H}_2\text{O}$ (gypsum), $2 \text{ MgO} \cdot \text{SiO}_2$ (enstatite), $\text{CaO} \cdot \text{SiO}_2$ (wollastonite), $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6 \text{ SiO}_2$ (orthoclase), $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6 \text{ SiO}_2$ (albite), $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6 \text{ SiO}_2$ (anorthite). The last three compounds

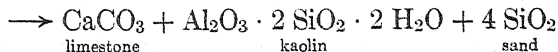
belong to a group of minerals called *feldspars*; these are present in large proportions in the enormous masses of granites and other igneous rocks of the earth's crust.

The weathering of granite. On page 27 granite was mentioned as a typical illustration of a *mixture*, since a granite may be a conglomerate (1) of a feldspar, (2) of quartz, and (3) of some micalike substance. Let us now take anorthite, $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6 \text{SiO}_2$, as an example of a feldspar, and try to guess what happened to it chemically during the last stages of the earth's cooling process (see p. 176). Let us suppose that the surface of the earth had cooled to about 200° . The water of our seas existed, therefore, at that time as water vapor, and there was enough of it in the atmosphere to exert a pressure of several hundred atmospheres on the earth's surface. Toward the top of the atmosphere (which must have been very cold then, just as it is today) the water vapor would condense to liquid and fall in terrific cloudbursts upon the earth, whence it would be boiled off again. This continued drenching helped appreciably in cooling things.

When the temperature dropped below 100° , water condensed and collected as a liquid in the low places of the earth's surface; and the seas were formed. The hot water dissolved all sorts of oxides from the rocks, all sorts of acids and bases were formed, and from them salts, in this gigantic test tube. Later many of the compounds became sedimentary deposits of minerals. Also present in the atmosphere was carbon dioxide gas, possibly to the extent of several atmospheres of pressure (as compared with 0.0003 of an atmosphere today). The carbon dioxide, under those extremely favorable conditions of temperature and pressure, attacked anorthite chemically and took out the lime, CaO , to form calcium carbonate, $\text{CaO} \cdot \text{CO}_2$, or CaCO_3 . What was left of the anorthite reacted with the hot water to form kaolin, which is the chief constituent of common clay.



anorthite



limestone

kaolin

sand

Our enormously extensive deposits of clay and limestone probably originated in some such fashion.

Incidentally, when the feldspar of a granite had been attacked, or weathered, as just described, the other two crystalline materials, the micalike substance and the quartz, were released mechanically from the conglomerate. After much physical pounding and battering the larger pieces of quartz were ground to sand. (Sand is silicon

dioxide.) Vast quantities of sand grains were matted together with mineral binding materials of various sorts, and beds of sandstone were thus laid down.

The search for minerals and the recovery of metals. Useful mineral bodies are found in igneous rocks, as well as in the deposits laid down by processes of sedimentation. They become available to us when they appear on the surface of the earth as "outcrops," although they are also located by drilling operations. It is the business of geologists and prospectors to find minerals. The form and structure of the crystalline minerals are studied by crystallographers; and chemists study their composition.

Several thousand native minerals are known, most of them complex oxides, and the larger part of these silicates. Few free metals are found in the native state, and only in relatively small amounts. It is the function of the metallurgist to recover the useful metals from their mineral compounds, usually in furnace operations of some sort, by *reducing* the metallic ions to neutral atoms.

Questions

1. (a) Sulfur constitutes 0.052 per cent of the earth's crust. State the relative percentages of aluminum and sulfur present in the earth's crust (see table, p. 176). (b) Sulfur costs about 1 cent per pound, while aluminum costs about 20 cents. Suggest reasons for this difference in price.

2. In how many different ways do oxides of metals differ from oxides of nonmetals?

3. What is the relationship between valence, atomic weight, and combining weight?

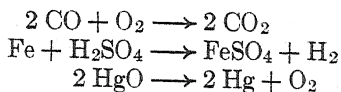
4. In the crystal lattice of sodium chloride, every sodium ion is surrounded by six chlorine ions, and every chlorine ion by six sodium ions (Fig. 99). Explain clearly why chemists assign a valence of 1 rather than of 6 to these ions.

5. Similarly, in the crystal lattice of calcium oxide (Fig. 122) the calcium ion and the oxygen ion each are surrounded by six ions of the other, and yet the chemist assigns a valence of 2 to each of these ions. Why?

6. (a) Define and illustrate oxidation and reduction of electrovalent compounds. (b) Do oxidation and reduction always occur together? Why?

7. (a) What are the valences of the following atoms when they exist as ions: Li, Ca, Na, Al, K, Fe, Cl, S, Mg, O, Cu, Br? (b) If the valences are variable, indicate what they are.

8. In the reactions expressed by the following equations, (a) what substances are oxidized? (b) what substances are reduced?



9. Write equations for reactions (a) in which a salt is formed along with water and (b) in which a salt is produced without the formation of water and in the total absence of water.

Problems

1. If 0.7600 g of magnesium combines with 0.500 g of oxygen, calculate the formula for the oxide produced. The atomic weight of magnesium is 24.32.

2. The approximate molecular weight of a gaseous compound of sulfur and oxygen is found by experiment to be 63. Chemical analysis shows the composition to be 50.05 per cent sulfur and 49.95 per cent oxygen. Deduce the exact formula, knowing the atomic weights.

3. Calculate the percentage composition of phosphorus trichloride, PCl_3 , and phosphorus pentachloride, PCl_5 .

4. How many electrons are lost (a) by 1 atom of calcium when oxidized to the ion? (b) by 1 g-at.wt of calcium? (c) by 1 combining weight of calcium? (d) by 1 g of calcium?

Reading References

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CHAPTER 12

Laws of Chemical Combination; Atomic Weights; Equations

Introduction. In the preceding chapters we have called attention to two of the laws of chemical combination (conservation of mass, definite composition), and have discussed atoms, ions, and molecules, and the writing of simple equations. We have shown how atomic weights and molecular weights can be determined, how percentage composition may be calculated, and how formulas for compounds may be deduced; and we have explained the meaning of such terms as *gram-atomic weight*, *gram-molecular weight*, *gram-equivalent weight*, and *valence*. We shall now collect and organize some of this material and expand it to some extent. Also, in this chapter, the chemist's method for determining exact atomic weight will be presented.

LAWS OF CHEMICAL COMBINATION

1. **The law of conservation of mass.** Lavoisier first demonstrated the law of conservation of mass, which may be stated thus: *Within the limits of experimental accuracy no change in the total mass of matter can be detected as a result of any chemical transformation which the matter may undergo.* Subsequent refinements of experimental methods have uniformly sustained the findings of Lavoisier. In 1906 Landolt at Berlin conducted a most critical test of this law. His general plan was to place the substances which were to act on each other (usually in solution) in the two limbs of a glass vessel of the form represented in Fig. 126. The open ends were then sealed and the vessel weighed. The vessel was then inverted to bring the substances into contact with each other, and, after the reaction, the vessel was again weighed. A large number of such experiments were carried out with every refinement of skill and apparatus, and very slight differences between the two weights were detected — never more than a few hundredths of a milligram in a total weight of

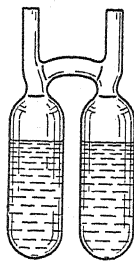


FIG. 126. Landolt's
Apparatus

100 g, or about 1 part in 10,000,000. These differences are to be attributed to unavoidable error.

2. The law of definite composition. Although the common experiences of the earlier chemists led them to believe in the validity of the law of definite composition, it was at one time (1802–1808) strongly contested by the distinguished Frenchman Berthollet. He believed that the composition of a substance is somewhat variable and depends on the relative quantities of the several materials present at the time of its formation. These views were opposed by a fellow countryman, Proust, who was professor of chemistry at Madrid during most of the controversy. Proust maintained that any apparent variability in the composition of a substance is due to lack of purity, and that when two elements form more than one compound, each of these compounds has its own exact composition and there are no intermediate gradations. Although Proust's experimental work, accurate as it was for those days, was subject to errors of from 1 to 2 per cent, the advance in experimental exactness through the years has steadily demonstrated the correctness of his conclusions. Within the limits of modern methods of analysis, then, we may state the *law of definite composition* thus: *A pure compound has a perfectly definite composition.*

3. The law of multiple proportions. Dalton (1805) first formulated the law of multiple proportions: *In those cases where two or more compounds are formed from the same two elements, A and B, if the compositions are stated not in percentages but in the different weights of the element A combined with a fixed weight of the element B, then these weights of A are in simple whole number ratio.* Wollaston (1808), a fellow countryman of Dalton, and Berzelius, a Swede (1811), quite independently of each other and of Dalton, observed these striking relationships. The composition of water and hydrogen peroxide conform to this law (p. 171), while the oxides of nitrogen are a particularly good group of compounds with which to illustrate it. If the nitrogen is calculated to a fixed weight (14.008 g) in these

OXIDE OF NITROGEN	PERCENTAGE COMPOSITION		COMBINING RATIO	
	Nitrogen	Oxygen	Nitrogen	Oxygen
Nitrous oxide	63.65	36.35	14.008	8
Nitric oxide	46.68	53.32	14.008	16
Nitrogen dioxide	30.45	69.55	14.008	32
Nitrogen pentoxide	25.94	74.06	14.008	40

different compounds, then the amounts of oxygen combined with 14.008 g of nitrogen are 8 g, 2×8 g, 4×8 g, and 5×8 g, respectively.

This is exactly what we might expect if nitrogen and oxygen atoms can unite in different ratios. The relationship is obvious when we write the formulas for these compounds: N_2O , NO , NO_2 , and N_2O_5 .

The atomic theory. Although we can speak today of the existence of atoms and molecules with so much assurance, chemists a hundred years ago had no such convincing proof as we now have. The atomic theory of Dalton (1805) (Fig. 127), an English schoolteacher, was really only a plausible hypothesis suggested to account for the facts of chemical combination known at that time. Throughout the development of modern chemistry this theory has had a dominant and controlling influence. Today, with the reality of atoms assured, the doctrine of the atomicity of matter is the basis of all chemical thought.



FIG. 127. John Dalton (1766–1844)

An Englishman famous as a teacher and scientist. He made many studies on the properties and composition of gases, but his greatest contribution to science was his development of the atomic theory. He wrote an important book entitled *A New System of Chemical Philosophy*, which exerted a great influence upon the development of chemistry

The three fundamental laws of chemical combination, (1) the law of conservation of mass, (2) the law of definite composition, and (3) the law of multiple proportions, are the concise statements of the vast body of chemical facts for which the atomic theory was designed to account.

The essential postulates of the atomic theory, together with a brief comment on the interpretation of chemical laws which the theory affords, are given here:

1. All matter is made up of minute bodies called atoms.
2. The atoms of an element are alike in mass, or in average mass, while the atoms of a different element have a different average mass.
3. The mass of an atom undergoes no change during chemical reac-

tion (except for loss or gain of electrons in ion reactions). This is a restatement of the law of conservation of mass in terms of atoms.

4. When one element combines with another, the *combination takes place between a definite small number of each kind of atom*. This assumption, together with postulate 2, explains how a given compound has of necessity a definite composition.

5. *Two kinds of atoms can unite in different ratios*. This postulate accounts for the law of multiple proportions.

THE CHEMIST'S METHOD OF DETERMINING ATOMIC WEIGHTS

Introduction. Already, early in this book, the physicist's method for determining the relative weights of the atoms, or atomic weights, has been described. The apparatus used in the positive-ray method is complicated, but the reasoning involved in reaching the conclusion is fairly simple. However, this method is a recent development, and the values which it yields for atomic weights have been available for chemists for only a few years. Long ago the chemist was able to deduce atomic weights by strictly chemical methods, although the reasoning was not simple, and no convincing conclusion was achieved until Cannizzaro had shown that Avogadro's hypothesis must be true (p. 76). The results obtained by the chemical method today are almost but perhaps not quite as accurate as those obtained with positive rays; but they are nevertheless, for most of the elements, extremely reliable. Let us now trace the logic employed by the chemist.

The chemist's deduction of approximate atomic weights. In the last chapter (p. 178) we saw, in the case of carbon dioxide, that if we know what elements are present in a compound and know (1) their atomic weights, (2) the molecular weight of the compound, and (3) the percentage composition, we can deduce (4) the formula. Here we have four things to deal with. If we know *three* of them, we can then deduce the fourth one:

1. Atomic weights	}	→ 4. Formula
2. Molecular weight		
3. Percentage composition		

Can we not turn the argument around, and if we know (2), (3), (4), deduce (1), namely, the atomic weights?

As a matter of fact, this is exactly the reasoning followed by a chemist; only he is handicapped in pursuing the argument because he does not have the *formula* of the compound either. In other words, he is dependent solely on (2) and (3). Experimental methods for determining (2) and (3) — (2) not very accurately and (3) very exactly — have been available for more than a hundred years. With only these two things known, the chemist can still reach a conclusion. Let us take a set of compounds, all of which we know to contain nitrogen, and find the atomic weight of nitrogen.

Procedure. We analyze these compounds to ascertain the percentage of nitrogen. The values are shown in the following table:

GASEOUS COMPOUND	PERCENTAGE OF NITROGEN BY ANALYSIS	APPROXIMATE MOLECULAR WEIGHT (22.4 l)	PART OF MOLECULAR WEIGHT DUE TO NITROGEN
Nitrogen gas	100.00	27.9	27.9
Nitrous oxide	63.65	44.1	28.1
Nitric oxide	46.68	30.0	14.0
Ammonia	82.24	17.1	14.1
Nitric acid	22.23	63.7	14.2
Cyanogen	53.74	52.2	28.1

We next determine the weight of 22.4 l (standard conditions) of the gas or vapor of each compound. These molecular weights are given in the third column. If we multiply the molecular weight of each compound by the percentage of nitrogen, *the product will be the portion of the molecular weight due to nitrogen* (fourth column). But since the molecules are made up of *atoms*, the part of a molecule due to nitrogen must represent the *sum of the weights of the nitrogen atoms present*. We notice that the numbers in the last column are very near either to 14 or to twice 14. If we examine a large number of compounds in this way, it is reasonable to expect that we shall find some that contain only one atom of nitrogen; and since we find none that gives a value of less than 14, we assume that 14 represents the approximate weight of a nitrogen atom.

The atomic weight is only approximate because, while the percentage compositions are accurate, the molecular weights, determined by the Dumas method, may be in error by several per cent (p. 79).

Thus the chemist can at least derive *approximate* atomic weights from percentage composition and molecular weight. In lieu of knowing the *formula* (4) for a compound, a whole series of compounds is studied, and the approximate atomic weight selected from the list.

Deduction of exact atomic weights. Now, for a given compound, we have the means for finding (1) approximate atomic weights, (2) approximate molecular weight, and (3) percentage composition, and can proceed as in the case of carbon dioxide (p. 178) to get the exact formula (4). This will be exact because only whole atoms occur in a molecule. If our calculated result is 0.97 of an atom or 3.05 atoms, we can be sure that the numbers are 1 atom and 3 atoms. Once we know the real formula of the molecule, we can then calculate the exact atomic weights from the percentage composition.

Example. We may take the gaseous compound nitrous oxide (laughing gas), listed in the table above, and calculate the atomic weight of nitrogen. Nitrous oxide contains only nitrogen and oxygen, and the atomic weight of oxygen is defined arbitrarily as exactly 16.000. The percentage composition for nitrogen is 63.65 (see table), and therefore for oxygen it is 36.35.

63.65 per cent of 44.1 (approx. mol. wt) = 28.1 = part of mol. wt due to nitrogen

36.35 per cent of 44.1 (approx. mol. wt) = 16.0 = part of mol. wt due to oxygen

But, since we have already selected *approximately* 14 as the atomic weight of nitrogen from the results of the table, and since we know that the atomic weight of oxygen is 16, it is obvious that the formula for nitrous oxide must be N_2O ; it contains 2 nitrogen atoms and 1 oxygen atom.

Now, working with 100 g of nitrous oxide, we know from the percentage composition that 63.65 g is nitrogen and 36.35 g is oxygen. These two exact weights must be in the same ratio as the exact weights of the 2 nitrogen atoms together and the 1 oxygen atom in the molecule. Therefore

$$\frac{63.65}{36.35} = \frac{x}{16.000}; x = 28.016, \text{ the exact weight of 2 nitrogen atoms}$$

Consequently the exact atomic weight of 1 nitrogen atom is 14.008.

Summary. These, then, are the steps taken to establish the exact atomic weight of an element by chemical methods:

1. Determine *accurately* by analysis the percentage composition of a number of compounds containing the element.
2. Determine the approximate molecular weight of the compounds.
3. From 1 and 2 calculate the part of the molecular weight due to the element in question. The smallest number so obtained will be the *approximate* atomic weight.
4. From 1, 2, and 3 get the exact formula.
5. From 1 and 4 calculate the exact atomic weight.

Thus far, in connection with the determination of molecular weight, we have described a method (Dumas) which is good only for gases and vapors. But later, general methods applicable to solids and liquids when dissolved in a solvent will be given. Solids and liquids which are sufficiently volatile can, of course, have their molecular weights determined in the vapor state.

The law of Dulong and Petit. As early as 1819 Dulong and Petit discovered a relationship between the atomic weights of *solid* elements and their specific heats. Their generalization was of some help in establishing approximate atomic weights of solid elements, once atomic weights for a few elements were known.

These investigators found that the atomic weight of a *solid* element multiplied by the specific heat gives an *approximate* constant whose value is about 6.4. This is called the *atomic heat* of the element. By the *specific heat* is meant *the quantity of heat required to raise the temperature of 1 g of a substance one degree*. Evidently the approximate atomic weight of an element is given by the equation

$$\text{Atomic weight} = 6.4 \div \text{specific heat}$$

The specific heat of a solid element varies considerably with the temperature at which it is measured. The following table gives some of the values accepted at the present time. With a few elements, notably boron, carbon, silicon, and beryllium, the value obtained deviates widely from the average under ordinary conditions, but approaches the normal value at high temperatures.

Table of Specific Heats and Atomic Heats at Ordinary Temperature

ELEMENT	ATOMIC WEIGHT	SPECIFIC HEAT	ATOMIC HEAT
Sodium	22.997	0.293	6.74
Magnesium	24.32	0.245	5.95
Aluminum	26.97	0.214	5.80
Phosphorus	30.98	0.202	6.26
Sulfur	32.06	0.203	6.51
Iron	55.85	0.112	6.26
Copper	63.57	0.095	6.04
Silver	107.880	0.057	6.15
Gold	197.2	0.0324	6.40
Mercury	200.61	0.0333	6.66
Lead	207.21	0.0315	6.53
Beryllium	9.02	0.410	3.70
Boron	10.82	0.250	2.70
Carbon (diamond)	12.01	0.141	1.69
Silicon	28.06	0.160	4.50

Atomic weights by the atomic-heat method. The manner in which the atomic heat has been helpful in finding atomic weights may be explained by an example. Suppose the atomic weight of magnesium is not known, and we want to know what it is. First, the specific heat of magnesium is measured and found to be 0.245. This divided into 6.4, the atomic heat, gives us at once an approximate value for the atomic weight, about 22. Then the gram-equivalent weight, or combining weight, of magnesium is obtained accurately, by careful analysis of one or more of its compounds. The result is 12.16 g. Since the exact gram-atomic weight is the exact gram-equivalent weight multiplied by some small whole number (valence), we see from the approximate atomic weight, 22, that this number is 2. Hence $2 \times 12.16 \text{ g} = 24.32 \text{ g}$, and this is the gram-atomic weight of magnesium.

Law of combining volumes (Gay-Lussac). In 1808 the eminent French chemist Gay-Lussac published the results of his experiments on the ratios *by volume* in which the gases known at that time combine. For example, he found that 2 volumes of hydrogen combine with 1 volume of oxygen to form 2 volumes of steam (p. 168), and that 1 volume of hydrogen combines with 1 volume of chlorine to form 2 volumes of the gas hydrogen chloride. As a result of many such studies he was able to make the following general summary, known as Gay-Lussac's law of volumes: *When two gases combine, there is a whole-number ratio between their volumes, and between the volume of either one of them and that of the product if it is a gas.*

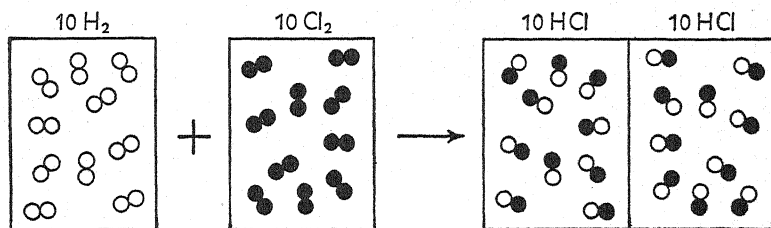


FIG. 128. Diagram Illustrating the Law of Gay-Lussac

Explanation of Gay-Lussac's law. Let us suppose that 1 tiny volume of hydrogen contains 10 molecules. Then 2 such volumes of hydrogen chloride must contain 20 molecules (Avogadro's principle). But each of these 20 molecules must contain *at least* 1 atom of hydrogen, or 20 in all; and these 20 atoms come from 10 molecules of hydrogen (Fig. 128). Consequently each molecule of hydrogen must contain *at least* 2 atoms. Similar reasoning shows that the molecules

of chlorine also must contain at least 2 atoms. Finally extension of these arguments to the equations

2 volumes hydrogen + 1 volume oxygen \longrightarrow 2 volumes water vapor
and

3 volumes hydrogen + 1 volume nitrogen \longrightarrow 2 volumes ammonia

shows that the molecules of oxygen and nitrogen are at least diatomic (contain two atoms).

This reasoning does not permit us to say that the molecules of the common elementary gases *are* diatomic. We can be certain only that the molecules of these gases contain 2 or 4 (or some other simple multiple of 2) atoms. We may for convenience assume that the simplest value is the correct one and see if there are any facts which are inconsistent with this conclusion.

The molecular weights of the elements. On several occasions we have previously found the molecular weights of elementary gases by calculating the weight of 22.4 l (under standard conditions) from the density of the gas. For hydrogen, oxygen, and nitrogen the molecular weights, thus obtained, are about 2, 32, and 28; and if we divide these by the respective atomic weights, we find that there are indeed 2 atoms per molecule, H_2 , O_2 , N_2 . By this test, the inactive rare gases are monatomic. The method may be extended to some of the less volatile elements, and involves weighing known volumes of their vapors at temperatures above the boiling points.

In this way it has been found that many metals are monatomic, K, Zn, Cd, Hg. The molecule of phosphorus contains 4 atoms, P_4 , up to a temperature of about 300° , but at 1700° it is P_2 . The molecule of sulfur is S_8 at ordinary temperatures, but at 1700° it becomes S_2 . With rising temperature the vibrations of the atoms within any molecule increase until large molecules break down into simpler ones. Even H_2 , O_2 , and N_2 can be thermally decomposed into atoms at sufficiently high temperatures.

EQUATIONS

Chemical equations. Before going farther, let us review some of the facts we have already learned about chemical equations and at the same time make some additions to what has been stated in earlier pages.

A chemical equation represents with symbols and formulas the rearrangement of atoms, ions, and molecules during a reaction. A

chemical equation merely expresses facts found out by experiment; it is a *shorthand* record of what actual substances enter into the reaction, and of what actual substances are formed. In other words, we cannot find out by equation-writing what the formula of a compound is or what changes the compound undergoes; but *having found out these facts*, we can express them by an equation.

Steps in writing an equation. The first step consists in writing, on the left of the arrow (\longrightarrow), the formulas or symbols of the starting substances (reactants), and, on the right, the formulas or symbols of the products of the reaction. The arrow symbol is usually read "gives" or "forms."

Example 1. Having learned that the formula of mercuric oxide is HgO , that it decomposes into mercury and oxygen on heating, and that the oxygen molecule is O_2 , while the mercury atoms remain single (p. 198), we express these facts as follows:

First step: $\text{HgO} \longrightarrow \text{Hg} + \text{O}_2 \uparrow$

The second and final step consists in *balancing the equation*; that is, we must adjust the coefficients of our equation (if necessary) so that there will be just as many atoms of each element on one side of the equation as on the other. Now in the equation above we have two atoms of oxygen (or 1 molecule) on one side of the equation. To get this amount of oxygen we must take 2 HgO , and this will give us 2 Hg as well as O_2 . Keeping in mind also the fact that the molecule and atom of mercury are identical (p. 198), we write the completed equation thus:

Second step: $2 \text{HgO} \longrightarrow 2 \text{Hg} + \text{O}_2 \uparrow$

Example 2. The combustion of iron:

First step: $\text{Fe} + \text{O}_2 \longrightarrow \text{Fe}_3\text{O}_4$

Second step: $3 \text{Fe} + 2 \text{O}_2 \longrightarrow \text{Fe}_3\text{O}_4$

Example 3. The decomposition of potassium chlorate:

First step: $\text{KClO}_3 \longrightarrow \text{KCl} + \text{O}_2 \uparrow$

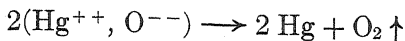
Complete: $2 \text{KClO}_3 \longrightarrow 2 \text{KCl} + 3 \text{O}_2 \uparrow$

Example 4. The reaction of nonmetallic oxide with water to form an acid:

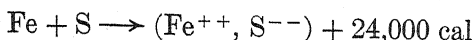
First step: $\text{P}_4\text{O}_{10} + \text{H}_2\text{O} \longrightarrow \text{H}_3\text{PO}_4$

Complete: $\text{P}_4\text{O}_{10} + 6 \text{H}_2\text{O} \longrightarrow 4 \text{H}_3\text{PO}_4$

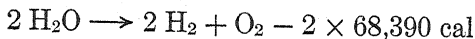
Conditions for a reaction not indicated by equations. Equations merely state the compositions and the weights of the substances taking part in a reaction. They do not tell the conditions under which the reaction will take place. For example, the equation



does not tell us that we must keep heating the mercuric oxide to a moderately high temperature in order to effect its decomposition. The equation



affords no indication that the reaction will not start at ordinary temperatures, though the large quantity of heat evolved suggests that, when once started, it will go on of itself. The equation

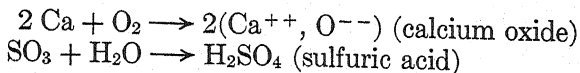


does not tell us how water may be decomposed, but merely that 36.032 g of water, when decomposed, will give 4.032 g of hydrogen and 32 g of oxygen, and that a great deal of energy (equal to 136,780 cal) is absorbed in the reaction. This energy must be supplied from some external source.

It will therefore be necessary to pay close attention to the details of the conditions under which a given reaction occurs, as well as to the statement of the equation itself.

Types of reactions. A study of the reactions so far considered shows that they may be classified into four general types, and we shall find that most of the reactions which we shall meet can be assigned to one of these four.

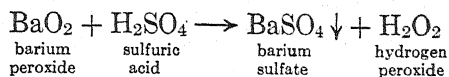
1. **Direct union.** Two elements (or compounds) may unite to form a compound. This is illustrated by the combustion of elements in oxygen, by the action of hydrogen upon different elements, and by the union of water with metallic and nonmetallic oxides to form acids and bases:



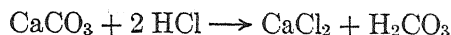
2. **Decomposition.** A compound may decompose into other compounds or elements, as is the case when mercuric oxide or potassium chlorate is heated.

3. **Substitution.** One element may take the place of another in a compound, setting the latter free. This is the case when the metals zinc and iron act upon hydrochloric or sulfuric acids, liberating hydrogen.

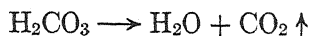
4. **Double decomposition.** This is probably the most common type of reaction and consists in the interchange of two elements present in two different compounds, thus resulting in the formation of two new compounds. It is illustrated in the equations which represent the reactions taking place in the preparation of hydrogen peroxide. In these reactions it will be seen that the barium of barium peroxide and the hydrogen of the acid change places, forming new compounds:



Another example is the action of hydrochloric acid on calcium carbonate:



The carbonic acid then decomposes to give carbon dioxide and water:



Molecular and ionic formulas. In equations the formulas for covalent compounds are written in the usual manner, as, for example, H_2O , NH_3 , CH_4 , unless there is good reason for indicating with structural formulas how the atoms within the molecule are connected. The formulas for *electrovalent compounds* are also generally written, by chemists, as if the compounds were *covalent*, NaCl , HgO , FeS , BaSO_4 , Al_2O_3 . Whether we use these simplest sets of *atoms*, or the simplest sets of *ions*, (Na^+ , Cl^-), (Hg^{++} , O^{--}), (Fe^{++} , S^{--}), (Ba^{++} , SO_4^{--}), (2Al^{+++} , 3O^{--}), depends largely on whether we are interested merely in showing the ratio of numbers of atoms, or whether we also wish to emphasize the electrovalent character of the compounds.

In any case, whenever a chemist employs such molecular formulas, instead of the more correct ionic formulas, to represent electrovalent compounds, *there is always in the background of his mind the realization that compounds of this sort are really built up of ions.*

Questions

1. State the laws of (a) conservation of mass; (b) definite composition; (c) multiple proportion. Illustrate each one by an example.
2. Explain clearly the various steps necessary to determine the exact atomic weight of an element.
3. What is the evidence that molecules of chlorine, oxygen, hydrogen, and nitrogen are diatomic, and should therefore be written as Cl_2 , O_2 , H_2 , and N_2 , rather than as Cl , O , H , and N ?
4. Does the law of Dulong and Petit hold for gases and liquids, as well as for solids?
5. (a) Write both the molecular formula and the structural formula of some compound and (b) state the information that each gives.
6. (a) Assuming that chlorine is univalent and that oxygen is bivalent, state the valence of each of the metals in the following compounds, assuming that the two elements in each compound are directly combined:

CaO , MgCl_2 , Al_2O_3 , PbO , AgCl , CuO , Fe_2O_3 , HgCl_2 , SnO_2

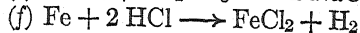
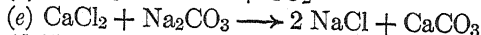
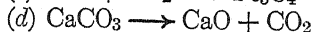
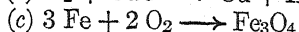
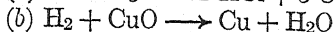
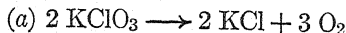
(b) Write the ionic formulas for these compounds.

7. The formulas of the oxides of certain metals are given below. These metals form chlorides. (a) Write the formula that you would naturally expect each of the chlorides to have.

Oxides:	MgO	Al_2O_3	SnO_2	Ag_2O	Au_2O_3	CuO
Chlorides:	?	?	?	?	?	?

(b) Write the ionic formulas for the chlorides.

8. Give the type of reaction represented by each of the following equations:



Problems

1. One liter of the compound propylene (gas), under standard conditions, weighs 1.89 g. It has the following composition: carbon, 85.62 per cent; hydrogen, 14.38 per cent. Calculate its formula.

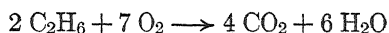
2. All the compounds listed in the table below contain carbon, and all are gases. (a) From the data given, calculate the molecular weight of each gas and the part of the molecular weight due to carbon. (b) From the results obtained, determine the approximate atomic weight of carbon. (c) Then calculate the exact formulas and finally the exact atomic weight of carbon.

NAME OF COMPOUND	WEIGHT OF 1 L OF THE GAS	PERCENTAGE OF CARBON PRESENT IN THE COMPOUND
Carbon monoxide	1.2504	42.85
Carbon dioxide	1.9768	27.27
Methane (contains C and H) .	0.7168	75.00
Acetylene (contains C and H) .	1.1621	92.30
Ethylene (contains C and H) .	1.2500	85.71

3. Carbon monoxide and carbon dioxide are both compounds of carbon and oxygen. From the percentage of carbon present in each, as given in the preceding table, show that the carbon and oxygen in these two compounds are combined in accordance with the law of multiple proportion.

4. The specific heat of aluminum is 0.22. Its combining weight is 8.99. Calculate (a) its approximate atomic weight, using the law of Dulong and Petit, and then (b) its exact atomic weight.

5. The gaseous compound ethane is inflammable and burns in accordance with the following equation:



(a) What volume of oxygen would be required to burn 1000 cc of ethane, both gases being measured under the same conditions of temperature and pressure? (b) How would the volume of carbon dioxide formed compare with the volume of ethane burned?

6. Compare the volume of oxygen required to burn a given weight of carbon with the volume of carbon dioxide formed, both gases being measured under the same conditions.

7. The compound commonly known as blue vitriol is a hydrate of copper sulfate (CuSO_4). It contains 36.06 per cent of combined water. Calculate the number of molecules of water present for each molecule of copper sulfate.

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CHAPTER 13

Atomic Number; the Periodic Law; Isotopes; Radioactivity

Introduction. Whenever one has to deal with a large body of related knowledge, one seeks to find some basis for classifying that knowledge. Thus we sort all natural objects into three kingdoms: mineral, vegetable, and animal. The first is nonliving; the last two are living. We may then establish subclasses. For example, we divide animals into two major divisions, vertebrates and invertebrates, depending on the presence or absence of a backbone. Vertebrates are further classified into fish, amphibians, reptiles, birds, and mammals, and each of these into families, and so on down to the individual species. Such classifications bring clearly into view the interrelations and differences among the various divisions of the subject. Chemistry too has its classifications. Probably the most significant of these is the periodic law, which concerns the characteristic chemical constituents of matter, namely, the elements and their structural units, the atoms.

Groups of elements. The study of the behavior of the chemical elements early demonstrated that there are groups, or families, of elements whose atoms have somewhat similar properties. We have seen that the inactive gases of the atmosphere are one such group. As an increasing number of elements became known, a great many plans of classification were suggested.

Classification based on chemical conduct. As soon as a reasonably clear distinction had been made between acids and bases, the elements were divided into two great classes, according to whether their oxides formed acids or bases on hydration, and were called respectively *acid-forming* and *base-forming* elements (or *nonmetals* and *metals*). Even such a broad classification was not free from difficulties, since many elements form more than one oxide; and it frequently happens, as with manganese and chromium, that some oxides of an element form acids, while others form bases. It may even happen that a given hydrated oxide may act both as an acid and as a base.

Method of finding relationships. A logical procedure is to select what seems to be a fundamental property common to all the indi-

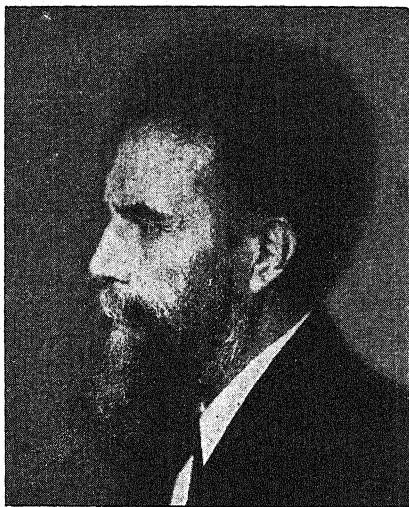


FIG. 129. *Wilhelm Konrad Roentgen*
(1845-1923)

Formerly director of the Physical Institute
at Würzburg, Germany

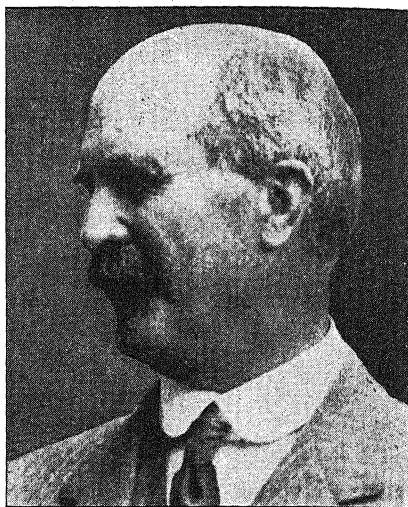


FIG. 130. *Sir William Henry Bragg*
(1862-)

He developed X-ray spectrum measure-
ments from crystal reflectors

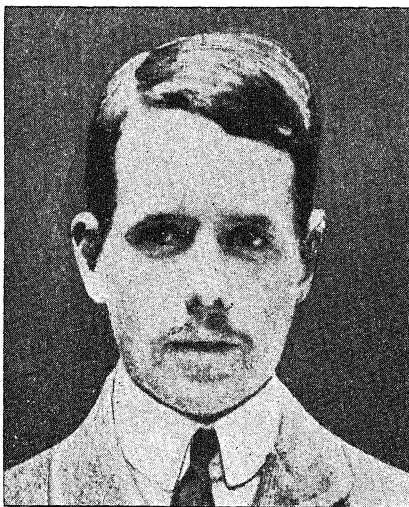


FIG. 131. *H. G. J. Moseley*
(1888-1915)

He proved that the properties of an atom
depend upon its atomic number



FIG. 132. *William David Coolidge*
(1873-)

The American scientist who invented the
most efficient X-ray vacuum tube

viduals of a group, to arrange them in the order in which this property increases, and to observe how other properties fall in with this order. For a long time chemists regarded the weights of the atoms as the most fundamental characteristic of the elements. Classifications based on increasing *atomic weights* were very satisfactory but showed a few inconsistencies. After the discovery of *atomic numbers*, it was found that classifications based on increasing atomic numbers did not have these inconsistencies. The atomic number is therefore the more fundamental property.

ATOMIC NUMBERS

X rays. The X rays were discovered by Roentgen (Fig. 129) in 1895, and some years later these X rays were shown to be just like visible light rays, only of much shorter wave lengths. In 1913, as a result of the work of Laue (p. 130) and of two English physicists, W. H. Bragg (Fig. 130) and W. L. Bragg, father and son, a reliable experimental method was developed for measuring accurately the X-ray wave lengths. Soon after this technique became available, a young Englishman, Moseley (Fig. 131), started a series of brilliant experiments.

Moseley's experiments. The essential feature of Moseley's apparatus was an X-ray tube, a modern form of which was devised by Coolidge (Fig. 132) and is known as the Coolidge tube (Fig. 133). The glass tube *T* is highly evacuated. The wire filament *B*, generally made of tungsten, is heated by a current from an electric battery to a bright-red heat. At such a temperature some of the electrons in the tungsten atoms are "boiled out," and they escape from the hot filament and form a cloud of electrons, which hovers around the filament. The electrons really *evaporate* from the filament, and we actually have come to speak of the *electron vapor pressure*.

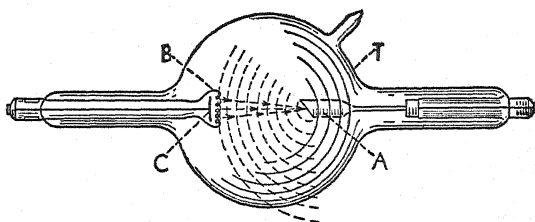


FIG. 133. Diagram of a Coolidge Tube

The metal cathode *C* is connected to the *negative* pole, and the target *A* to the *positive* pole, of a suitable source of direct current. As a result of the repulsion at *C* and attraction at *A*, the electrons are caused to travel at high velocity, like so many bullets, across the

vacuous space and to bombard the target *A*. The atoms in the surface of the target, under bombardment by electrons, give off X rays. Now what Moseley did was to place targets made of different metals in the tube and measure the wave length of the X rays given off. He found that when the voltage across *C* and *A* was made sufficiently large, every one of the different metals gave an X-ray spectrum which distinguished the atoms of that metal from the atoms of all other metals. Since Moseley's death practically all the elements (with the exception, of course, of the rare gases), either in elementary form or in the form of their compounds, have been made into targets and their characteristic X-ray wave lengths measured.

Atomic number. The X-ray spectra of the elements found by the Moseley method may be arranged in a series. When this is done,

Ti (22)			
V (23)			
Cr (24)			
Mn (25)			
Fe (26)			
Co (27)			
Ni (28)			
Cu (29)			

FIG. 134. Decrease of X-Ray Wave Lengths (toward the Left) with Increasing Atomic Number

there is a gradual and uniform change in the position of the lines from hydrogen (lines of longest wave length) to uranium (lines of shortest wave length) (Fig. 134). Although the X-ray spectra of the rare gases cannot be determined, there are breaks in the series corresponding to the expected position of these elements. The serial numbers H (1), He (2), Li (3), Be (4), . . . , U (92) assigned to the elements when arranged in the order suggested by their X-ray spectra are called *atomic numbers*. It is

true that there are a very few gaps, corresponding to elements of uncertain discovery; but when these elements present their authentic credentials, they will unquestionably be seated in their proper places. In fact, X-ray spectroscopy has played an important part in proving the existence of several of the recently discovered elements. Further, since hydrogen is the lightest and uranium the heaviest element, we assume that the total number of elements to be expected is ninety-two.

In the following chapter, we shall find that the atomic number of an element also represents the electric charge (positive) on the nucleus of an atom of the element.

THE PERIODIC LAW

Introduction. The great generalization known as the periodic law may now be stated thus: *The physical and chemical properties of the elements are periodic functions of their atomic numbers.* In other words, if the elements are arranged in order of their increasing atomic numbers, the variation of the properties of the elements follows a recurring cycle much like the seasons, sunspot activity, and business conditions. The usefulness of the periodic law is not that of a mathematical equation but is rather of qualitative and suggestive character. In order to see the periodic relationships among the elements clearly, we need some visual method of representation. Such representations may take the form of *periodic tables* (pp. 210 and 213). Many different periodic tables have been suggested, but a modified form of the original table proposed by the Russian chemist Mendeléeff (Fig. 136) in 1869 is most commonly used.

General plan of arrangement. Every periodic table contains rows, or *periods*, of elements. If hydrogen is omitted, the first eight elements in the order of their atomic numbers are

2	3	4	5	6	7	8	9
He	Li	Be	B	C	N	O	F

These elements all differ markedly from each other and constitute the first row, but the tenth element, neon, is very similar to helium. It is placed just below the latter, and a new row follows:

10	11	12	13	14	15	16	17
Ne	Na	Mg	Al	Si	P	S	Cl

The next element, argon, again resembles helium and neon, and begins a third row:

18	19	20	
A	K	Ca	etc. as given in the periodic table.

An inspection of the elements in the eight *vertical* columns (or *groups*) brings to light a remarkable fact. Not only are helium, neon, and argon very similar, but a more or less pronounced resemblance is found among the several elements in each of the columns. Thus lithium, sodium, and potassium are very similar, as are beryllium, magnesium, and calcium.

The relationship of properties to atomic numbers. A consideration of the valences of the first twenty elements will demonstrate not only the resemblances among elements in the same vertical column but also the gradual changes encountered as one goes suc-

The Periodic Arrangement of the Elements according to Atomic Numbers

Type of hydride	RH	RH ₂	RH ₃	RH ₄	RH ₅	RH ₂	RH ₃	RH ₄	RH ₅	RH ₂	RH	RO ₄
Type of oxide	R ₂ O	RO	R ₂ O ₃	RO ₂	R ₂ O ₅	RO ₃	R ₂ O ₅	RO ₂	RO ₃	RO ₃	R ₂ O ₇	RO ₄
PERIOD	GROUP 0	GROUP I	GROUP II	GROUP III	GROUP IV	GROUP V	GROUP VI	GROUP VII	GROUP VIII	GROUP VIII	GROUP VIII	GROUP VIII
0		H = 1.0080										
1	He = 4.003	Li = 6.949	Be = 9.02	B = 10.82	C = 12.010	N = 14.008	O = 16.000	F = 19.00				
2	Ne = 20.183	Na = 22.997	Mg = 24.32	Al = 26.97	Si = 28.06	P = 30.98	S = 32.06	Cl = 35.457				
3	A = 39.944	K = 39.096	Ca = 40.08	Sc = 45.10	Ti = 47.90	V = 50.95	Cr = 52.01	Mn = 54.93	Fe = 55.85	Co = 58.94	Ni = 58.69	
4	Kr = 83.7	Rb = 85.48	Sr = 87.63	Y = 88.92	Zr = 91.22	Cb = 92.91	Mo = 95.95	Ma = ?	Ru = 101.7	Rh = 102.91	Pd = 106.7	
5	Xe = 131.3	Cs = 132.91	Ba = 137.36	Rare Earths	Hf = 178.6	Ta = 180.88	W = 183.92	Re = 186.31	Os = 190.2	Ir = 193.1	Pt = 195.23	
6	Ra = 222	Au = 197.2	Hg = 200.61	Tl = 204.39	Pb = 207.21	Bi = 209.00	Po = (?)	At = 210				
			Ra = 226.05	Ac = ?	Th = 232.12	Pa = 231	U = 238.07					

* The atomic numbers are printed in red, and the atomic weights in black. In Group III, upper row of Period 5, we find a number of elements of atomic numbers 57 to 71 inclusive. These are known as the *rare-earth elements*. They closely resemble each other in properties and do not fit well into a simple table. Their atomic numbers, symbols, and atomic weights are as follows: (57) La, 138.92; (58) Ce, 140.13; (59) Pr, 140.92; (60) Nd, 144.27; (61) Sm, 150.43; (62) Eu, 152; (63) Gd, 156.9; (64) Tb, 158.92; (65) Dy, 162.46; (66) Ho, 164.94; (67) Er, 167.2; (68) Tm, 168.93; (69) Yb, 173.04; (70) Lu, 174.99.

† The discovery of elements of atomic numbers 85 and 87 has been claimed but lacks confirmation.

cessively from one column to another. The typical oxides of these elements are

He (none)	Li ₂ O	BeO	B ₂ O ₃	CO ₂	N ₂ O ₅	—	—
Ne (none)	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₃	Cl ₂ O ₇
A (none)	K ₂ O	CaO					

The hydrogen compounds do not show the same gradual increase all across the table but instead exhibit a rise and fall. However, the same pattern is followed by each horizontal row:

He (none)	LiH	—	BH ₃	CH ₄	NH ₃	H ₂ O	HF
Ne (none)	NaH	—	—	SiH ₄	PH ₃	H ₂ S	HCl
A (none)	KH	CaH ₂					

Paralleling these regularities in valence, there is a gradual change in the chemical behavior of the elements. Helium, at the beginning of the first row (Group 0), is a gas with no chemical activity at all. Lithium is a metallic element of very strong base-forming character. Beryllium is also a metal, but with less strongly marked base-forming character. Boron is a metalloid (semimetal) and is much more acid-forming than basic in character. In carbon all basic properties have disappeared, and it is an acid-forming element exclusively. The succeeding elements, nitrogen, oxygen, and fluorine, are increasingly acid-forming.

Long and short periods. Between the rare gases helium and neon and also between neon and argon, there are seven elements. Between the rare gases argon and krypton and krypton and xenon, there are seventeen elements; and between xenon and radon, thirty-one. This situation introduces complications into the periodic classification and makes it necessary to spread some of the periods over two horizontal rows. The first two rows, already described, are called the *short periods* of 8 (He-Ne, Ne-A). It will be noted in the table (p. 210) that in order not to interrupt the regularities of the fourth row, the three elements following manganese (in the third row), namely, iron, cobalt, and nickel, which resemble each other very closely, are set aside in a separate ninth column. Together, the third and fourth rows make up the first long period (A-Kr, period 3). The fifth and sixth rows duplicate in pattern the third and fourth and constitute the second long period (Kr-Xe, period 4). The *very long period* (Xe-Rn, period 5) containing thirty-two elements resembles the two long periods with the exception that there are fifteen rare-earth elements (atomic numbers 57-71) in group 3 instead of a single element. This anom-

alous situation is in strict accord with chemical behavior because all the trivalent rare earths are so closely related that their separation is extremely difficult. The final period is incomplete.

Two families in a group. A study of the elements within a group discloses a further fact of much interest. As we have seen, the relationship between the corresponding elements in Periods 1 and 2 is a very close one. Below this point the elements in each group (except in Groups 0 and VIII) fall very naturally into two subgroups called *families*. In the table these are designated *A* and *B*. The elements in one family resemble each other much more closely than they do those in the other family in the same group. Thus, in Group II, calcium, strontium, barium, and radium form one family of very similar elements, while zinc, cadmium, and mercury constitute the other.

The elements of the first two rows (or periods), which include the sixteen elements of smallest atomic weight, do not fall distinctively into either family in their group, but combine the properties of both families. So they stand as types of the general characteristics of their groups.

Group and family resemblances. We have already seen that the elements in any one group have much the same valence characteristics. Consequently they form oxides, hydroxides, acids, and salts of the same general formula. The hydrides and oxides of *maximum* valence are indicated by the formulas at the top of the columns (p. 210). It usually happens that, in addition to the oxide characteristic of a group, each element forms other oxides not predicted by the table. The resemblances of the members of a family to each other are more marked, and extend not only to the general chemical characteristics but to physical properties as well. There is, in most cases, a more or less regular variation in any given property as we pass from the member of smallest atomic number to that of largest, so that the middle one is a mean between the others. This is true in regard to chemical activity and such properties as melting point, boiling point, density, color, solubility of analogous salts, and many similar properties. These points will be dwelt upon in the several families as they are taken up in order.

Thomsen's table: the long-period system. The Danish chemist Thomsen suggested an arrangement of the periodic table which, with a number of modifications, is shown below. The numeral below the symbol of the element is its atomic number. Hydrogen and helium form a first row of two elements. This is followed by the two short periods of eight elements each. Then follow the three long

periods of eighteen elements each, and an incomplete period. The diagonal lines connect the elements of the short periods with the two families of their groups. In this table *those elements that are most intimately related fall in the vertical columns formed by the long periods.*

Thomsen's Table of the Elements

									H								
									1								
									Li	Be	B	C	N	O	F	Ne	
									3	4	5	6	7	8	9	10	
									Na	Mg	Al	Si	P	S	Cl	A	
									11	12	13	14	15	16	17	18	
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
Rb	Sr	Y	Zr	Cb	Mo	Ma	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	—	Rn
55	56	57	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86
—	Ra	Ac	Th	Pa	U												
87	88	89	90	91	92												

The work of Lothar Meyer. Whereas Mendeléeff compiled his periodic table on the basis of recurring chemical behavior, Lothar Meyer discovered a periodicity among the physical properties of the elements. In particular, he was interested in the atomic volumes (atomic weight/density) of the elements. On plotting the values for the atomic volumes of the elements against their atomic weights, he did not obtain a smooth curve but one that rose and fell, somewhat in the manner of crests and troughs of water waves (Fig. 135). Elements of similar valence and chemical conduct occupy corresponding positions on the ascending or descending portions of the curve. Similar rising and falling curves are obtained by plotting the numerical values of other physical properties, such as melting and boiling points, hardness, conductivity toward heat and electricity, compressibility, and the size of ions in crystals. A significant fact brought out by the atomic volume and similar curves is that the length of the period increases from 8 to 18 and finally to 32 in harmony with what we have already said concerning the periodic table.

General usefulness of the periodic table. The periodic table is of great service to chemists in a number of ways.

1. *Checking and stimulating experimental work.* The periodic table gives a constant check on experimental work. If a given piece of work results in a value which is not in harmony with the table,

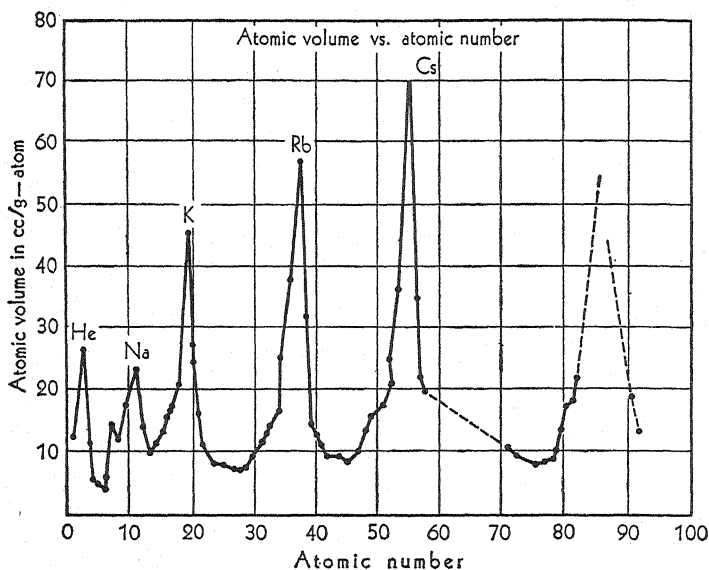


FIG. 135. Curves Showing Periodicity of Atomic Volumes when Plotted against the Atomic Number

attention is at once directed to the value, and it is very carefully checked. In a similar manner, predictions of properties or reactions may be made on the basis of the periodic table and then verified by experiment.

2. *Predicting and challenging new elements.* The table has also been of value in forecasting the discovery of new elements. From the position of vacant spaces and from the character of the elements on each side of them, the properties of the missing elements can in a measure be predicted. Shortly after the announcement of the periodic law, the elements scandium, gallium, and germanium were discovered and were found to have the properties predicted by Mendeléeff. The remarkable accuracy of these predictions went far to win general acceptance of the periodic law. On the other hand, the table has been of much service in ruling out a number of supposed elements for which there is no place.

3. *Assisting the memory.* Finally, from the standpoint of convenience, the table is of much service in assisting the memory. Instead of attempting to remember the characteristics of the elements

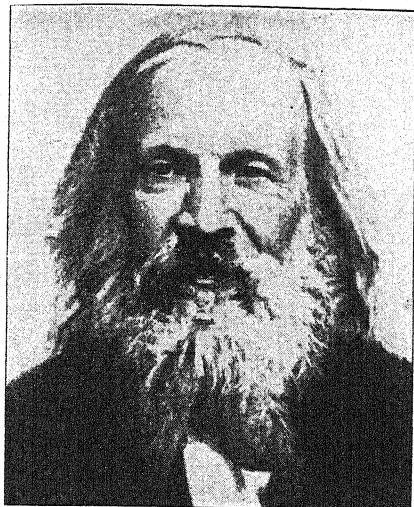


FIG. 136. *D. I. Mendeléeff*
(1834-1907)

A Russian chemist who is noted chiefly for proposing the periodic classification of the elements



FIG. 137. *F. W. Aston*
(1877-)

© Elliott & Fry

Professor of physics in the Cavendish Laboratory, Cambridge, England

in detail, one remembers those of a few typical elements and associates with them the characteristics of the others, keeping in mind the variations common throughout the periodic table.

Irregularities in the table. Notwithstanding the many very striking relationships suggested by the periodic grouping, it contains a number of imperfections and anomalies.

1. In the first place, the relationships are only qualitative in character, so that no property of one element can be calculated more than approximately from the known magnitude of the same property in other elements.

2. It is a most striking fact that there is no place in the table for hydrogen, one of the most important of all the elements. It seems to stand quite alone and to have no close relationship to any other element.

3. The last column in the table is unlike any of the other groups.

4. Some of the families of the same group do not always show the close resemblance that might well be expected. Thus copper, silver, and gold are very different in many respects from the alkali metals with which they are included in one group.

5. In all but three cases the order of the atomic numbers and that

of the increasing atomic weights are the same. In the case of argon and potassium, tellurium and iodine, cobalt and nickel, this is not true; for the element of smaller atomic number has the larger atomic weight.

While these irregularities are somewhat troublesome, they do not diminish the usefulness of the periodic table. Further, we shall find that almost all these irregularities have a perfectly logical explanation.

ISOTOPES

Atomic weights and atomic numbers. Why is it that the atomic weights, in contrast to the atomic numbers, are often fractional values? In some cases the difference between the atomic weights for successive elements is very small, as between cobalt and nickel, while in others it is as much as five units, as between calcium and scandium. Why do not the atomic weights differ regularly from element to element? Before we pass along to other subjects, we must seek at least partial answers to these questions.

Prout's hypothesis. Soon after the atomic theory was advanced (Dalton, 1805), the English physician Prout suggested that all elements are really multiples of hydrogen, and that accurate determinations of atomic weights would show that they are whole numbers, based on hydrogen as unity. This hypothesis stimulated a great deal of splendid work; but the results all went to show that many weights are fractional, and the hypothesis was abandoned.

Positive rays; mass spectrum analysis. We have seen that atomic weights can be determined by positive-ray analysis, a method in-

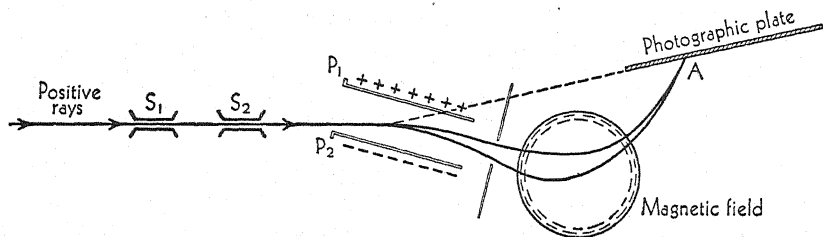


FIG. 138. *Diagram of a Mass Spectrograph*

Positively charged ions, formed in a chamber to the left by bombardment of volatilized atoms by electrons, enter the mass spectrograph through the slits S_1 , S_2 . The streaming ions are bent downward toward the negative plate P_2 , but the slower ions of a given charge and mass are bent more than the fast ones. The divergent beam enters the magnetic field (with its lines of force running down into the plane of the paper, north pole to south pole) and is bent upward. The electric and magnetic fields, working in this way, cause all ions of given charge and mass to converge at the spot A on the photographic plate, no matter what the velocities may be

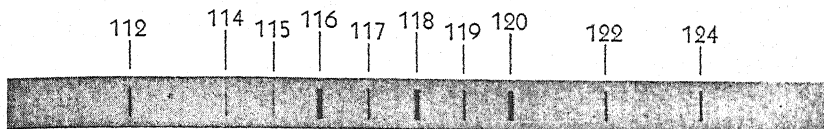


FIG. 139. A Mass Spectrogram Showing the Isotopes of Tin

Photographed by K. T. Bainbridge and E. B. Jordan, Harvard University

vented by Thomson and perfected by Aston. The only difference between the apparatus described here and that described previously (p. 47) is the introduction of a magnetic field, the purpose of which is to bring all the positive ions of a given ratio of charge to mass to a single focus on the photographic plate, *regardless of the speed of the ions*. The details of the method are shown in Fig. 138. From the position of the spots or lines on the plate the relative weights of the particles can be calculated. Because such a plate when developed resembles in many respects a spectrum photograph, it is frequently called a *mass spectrogram* (Fig. 139), and the method is known as *mass spectrum analysis* or *mass spectroscopy*.

Results of mass spectrum analysis; isotopes. Practically all known elements have been submitted to mass spectrum analysis. In the majority of cases it has been found that the atoms of a given element do not all possess exactly the same weight; for example, neon (atomic weight = 20.183) is made up of three varieties of atoms having the masses 20, 21, and 22; nitrogen (atomic weight = 14.008), of atoms of masses 14 and 15; iron, of four varieties of atoms (54, 56, 57, 58). However, there are a number of elements, such as helium, sodium, phosphorus, iodine, and bismuth, all of whose atoms do have the same atomic weight, in accordance with the belief of Dalton. The different varieties of atoms of a given element (those with different masses) are called *isotopes* of that element. The isotopes of all the elements have masses either exactly equal to whole numbers or so nearly so that they are commonly regarded as having such masses (see Table of Isotopes in Appendix).

The percentage of isotopes of an element. Because the individual isotopes of a given element are not present in equal amounts, the *intensities* of the lines on a mass spectrogram are not the same. By measuring the intensities of these lines, it is possible to make a very accurate estimate of the *relative numbers* of the different isotopes which go to make up an element. For example, the relative abundance of the three isotopes of neon is as follows: for 20, it is 90.4 per cent; for 21, it is 0.6 per cent; and for 22, it is 9 per cent. This is in good agreement with the atomic weight of 20.182 obtained by other methods. With a knowledge of the weights of the

various isotopes of an element, together with the relative amounts of each, it is easy to calculate the atomic weight of that element. In this manner, Aston has determined atomic weights, in some cases, with an accuracy of 1 part in 10,000. It is gratifying to know that his determinations and those made by highly refined chemical methods (Chap. 12) agree very well. Thus it is evident that in nature the isotopes of an element are already mixed together and that the atomic weight is simply the average weight of a mixture of isotopes in a definite ratio. This is the reason why atomic weights are often fractional values, whereas the isotope weights are whole numbers.

Separation of isotopes. Since the mass spectrograph is essentially a device for sorting out the various isotopes of an element, one immediately wonders if it is not possible to use a mass spectrograph to obtain samples of pure isotopes. So far this has not proved to be practical, largely because the quantities of isotopes collected are so very small. However, a few other methods have been found for effecting at least a partial separation of isotopes. In connection with radioactivity (pp. 220–225) we shall see how it is possible to obtain small amounts of individual isotopes of some of the elements in relatively pure condition. In general, it is not an easy matter to *unmix* the isotopes to any appreciable extent. Such a separation can be partially accomplished, however, by diffusion processes, that is, by resort to the principles involved in *Graham's law* (p. 72).

Isotopes of hydrogen. It has been proved by spectroscopic methods, that hydrogen has three isotopes of mass about 1 (named protium), 2 (deuterium), and 3 (tritium) respectively. The isotope of mass 2 was discovered by Professor Urey (Fig. 140) of Columbia University and his co-workers. It is present in ordinary hydrogen to the extent of only about 1 in 6000 parts, while that of mass 3 is present in much smaller percentages — 1 part in several millions.

Deuterium oxide (heavy water). Chemists have long regarded pure water as represented by the formula H_2O , in which each of the hydrogen atoms present has an atomic weight of 1. With the discovery of the heavier isotopes of hydrogen extensive experiments were carried on in the hope of obtaining the corresponding compound in which each of the hydrogen atoms present has an atomic weight of 2. This compound has now been obtained and is known as deuterium oxide or commonly as *heavy water*. There is about one part of heavy water present in 6000 parts of ordinary water. When ordinary water is electrolyzed, the lighter product is acted upon proportionately to a greater extent than the heavier product. The residues are therefore richer in heavy water, and by repeating the process the pure product can be obtained. While heavy water has all the appearance of ordinary water, it is markedly different from it in many of its properties. It is hygroscopic, boils at 101.42° , freezes at 3.8° , and its

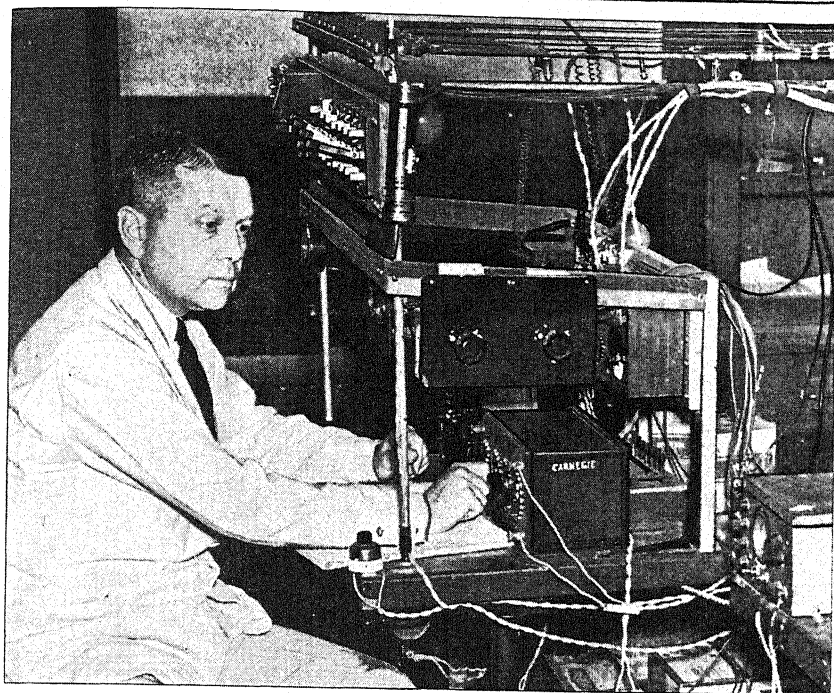
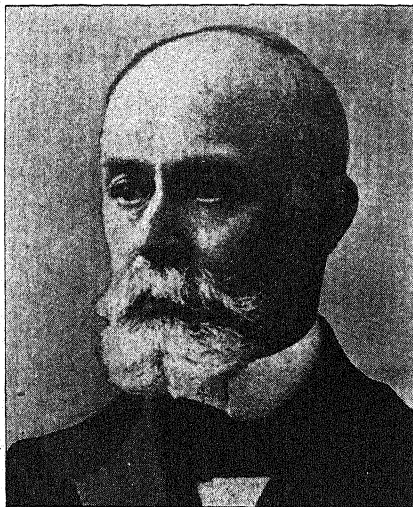


FIG. 140. *Harold C. Urey in His Laboratory at Columbia University*
He was awarded the Nobel prize in 1934 for his discovery of the isotope of hydrogen of atomic weight 2

maximum density is at 11.6° . It is claimed that seeds do not germinate and low forms of life do not thrive when immersed in it.

Isotopes and the definition of an element. The discovery of isotopes raised some question as to the definition of an element. Was each isotope to be considered as a separate element, or was this latter term to be retained in more nearly its original meaning? An answer may be given in terms of atomic numbers and chemical behavior. If we examine the chemical properties of two isotopes of the same element (same atomic number), we find that any differences in chemical behavior are so minute that they are barely detectable. When two such materials are mixed, they *cannot be separated* by chemical methods, except with the greatest difficulty, and then only in the case of the very light elements. Further, isotopes of a particular element also have the same physical properties, except for those which depend on mass. Because of these facts we may best define an element as *a substance all of whose atoms have the same atomic number.*



Science Service

FIG. 141. *Antoine Henri Becquerel*
(1852–1908)

French physicist. Late professor of physics in the laboratory of the National Museum of Natural History in Paris. He made many discoveries in the field of optics. In 1896 he discovered that radiographs could be produced by uranium salts similar to those produced by X rays. It was this discovery that suggested to Monsieur and Madame Curie the investigations that later led to the discovery of radium and polonium. In 1903 the Nobel prize for physics was divided between Monsieur Becquerel and Monsieur and Madame Curie



FIG. 142. *Madame Marie Curie*
(1867–1934)

Late professor in the Sorbonne, Paris. Born in Warsaw, Poland, Madame Curie, together with her husband, Pierre Curie, discovered polonium in July, 1898, and radium in December, 1898. Monsieur Curie was killed in a street accident in 1906. Madame Curie continued the investigations, isolating pure radium, studying its properties, and determining its atomic weight. Recipient of the Nobel prize for chemistry, 1911. Elected honorary member of the American Chemical Society in 1909

RADIOACTIVITY

Radioactivity and its discovery. In the year 1896 the French physicist Becquerel (Fig. 141) discovered that the metal uranium, as well as its compounds, possesses a property that has become known as *radioactivity*. A little later it was found that minerals containing uranium, notably *pitchblende*, U_3O_8 , are as much as three to four times as radioactive as the pure metal. This fact led Madame Curie (Fig. 142) and her husband Pierre Curie to the discovery of *radium*, which was found to be present in uranium minerals but in exceedingly small percentages. The property of radioactivity was found to be due to the spontaneous disintegration of the heavy atoms of

uranium and radium to form entirely different atoms — a sort of natural "transmutation" of matter. The disintegrations are ac-

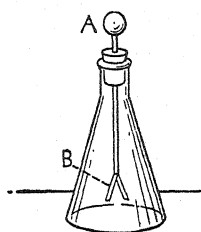


FIG. 143. *A Charged Electroscope*

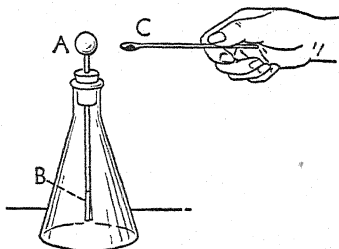


FIG. 144. *An Electroscope Discharged by Uranium Radiations*

companied by the emission of so-called rays. These rays have some remarkable properties. (1) They *affect a photographic plate*; indeed, Becquerel discovered radioactivity in this way. He put a specimen of a uranium compound in a thin metal tray and placed the tray on the film side of a photographic plate wrapped in black paper; and he found later that the plate when developed had been affected *through* the thin metal, as though exposed to light. (2) The rays will also *discharge an electroscope*; or rather the *ions*, which are produced in air through which the rays are passing, will conduct the charge away from the electroscope. This is shown by the collapse of the electroscope leaves *B, B* (Figs. 143, 144) by radioactive material *C*.

Rutherford's experiment. In a very simple experiment Rutherford (Fig. 150) proved the existence of three types of rays, which he named alpha (α), beta (β), and gamma (γ) rays. He placed a small quantity of a material containing radium at the bottom of a hole bored in a piece of lead (Fig. 145). All rays were stopped, by the shielding power of the lead, except those headed directly upward. He then placed the radium between the poles of a magnet, as shown, with a photographic plate (protected from light) arranged above to receive the rays. One kind of ray, the gamma ray, was not bent in the magnetic field; but the alpha ray and the beta ray were deflected from their course, in opposite directions and to different degrees, as shown in a general way in this figure. From this extent of deflection in the magnetic field it is possible to calculate the masses and charges of the two kinds of particles of which the alpha rays and beta rays consist.

Nature of the rays. The alpha rays (or, really, alpha particles) are *helium ions*, each one bearing two positive charges of electricity (de-

ficient in two electrons). They are shot off with velocities varying from 9000 to 14,000 miles per second, but cannot penetrate the

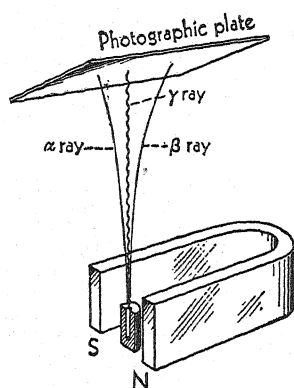


FIG. 145. Showing the Behavior of Radioactive Rays in a Magnetic Field

thinnest sheets of metal and are stopped even by a sheet of paper. They have little action on the photographic plate. The beta rays (or particles) are *electrons* and are shot off with a velocity of approximately 100,000 miles per second. They are the same as the cathode rays of a vacuum tube. They have greater penetrating power than the alpha rays but are stopped by relatively thin sheets of metal. The gamma rays are light, of extremely short waves, resembling X rays. They can penetrate relatively thick layers of metal, and can be detected by the electroscope after traversing 8 or 10 in. of lead. Both beta rays and gamma rays affect a photographic plate.

The relative penetrating power of the three types of rays, tested toward aluminum, are approximately as follows: alpha rays, 1; beta rays, 100; gamma rays, 10,000.

Radioactivity a series of decompositions. It is not to be thought that the atoms of uranium or radium explode into alpha, beta, and gamma rays and nothing else. Rather the original atom gives rise to a *series* of changes, one after the other, in each of which one or more kinds of these rays are given out, and a new kind of atom is formed. These changes cease when they result in a new atom that is stable and not radioactive. The atoms of the element uranium are the starting point in this series of changes, and those of radium are among the most stable (slowest to change) of all atoms in the series.

The uranium disintegration series. There are several isotopes of uranium, but it is the one of mass 238, usually designated as U I, that is the starting point in the uranium series of radioactive changes, as shown in the table on page 223.

Beginning with uranium I disintegration proceeds by successive steps, passing through uranium X_1 to uranium X_2 and so on to the final product, lead, with radium as one of the intermediate products. Such a series is known as a disintegration series and reminds one of the generations in human life — great-grandmother, grandmother, mother, daughter. Uranium I, then, is the great-great-great-grandmother of radium and the original ancestor in the whole radium lineage.

Table of Uranium Series

NAME	SYMBOL	ATOMIC WEIGHT	ATOMIC NUMBER	ISOTOPE	RADIATION	HALF-LIFE
Uranium I . . .	UI	238	92	U	α	4.67×10^9 yr
Uranium X ₁ . .	UX ₁	234	90	Th	β	24.6 days
Uranium X ₂ . .	UX ₂	234	91	Pa	$\beta(\gamma)$	1.15 min
Uranium II . . .	UII	234	92	U	α	2×10^6 yr
Ionium	Io	230	90	Th	α	6.9×10^4 yr
Radium	Ra	226	88	Ra	$\alpha(\beta + \gamma)$	1690 yr
Radon	Rn	222	86	Rn	α	3.85 days
Radium A	RaA	218	84	Po	α	3 min
Radium B	RaB	214	82	Pb	$\beta(\gamma)$	26.8 min
Radium C	RaC	214	83	Bi	β	19.5 min
Radium C'	RaC'	214	84	Po	α	10^{-6} sec
Radium D	RaD	210	82	Pb	β, γ	16.5 yr
Radium E	RaE	210	83	Bi	β	5 days
Radium F	RaF	210	84	Po	$\alpha(\gamma)$	136 days
Radium G (lead)	RaG	206	82	Pb		Infinite

Some of the transformations take place very rapidly, others slowly; but the rate seems not at all affected by external conditions, such as temperature (no matter how high or low). It is convenient to state the rate of change in terms of the *half-life*, that is, the time required for half of any given weight to change. The more rapid the decay, the greater is the energy with which the rays are emitted. Heat is also liberated. For instance, 1 g of radium hourly evolves about 134 cal of heat. The total heat given off in a calorimeter by the complete disintegration of 1 g of radium would be something like 350,000 times the heat of combustion of 1 g of carbon.

Radioactive elements and the periodic table. The table (Fig. 146) shows the positions of the members of the uranium disintegration series in the periodic table. The loss of one alpha particle results in a lowering of atomic number two units and a shift to the left in the table of two places. With beta-particle emission there is a gain of one in the atomic number and a shift to the right of one place. The changes in atomic weight are indicated vertically.

Note that every vertical column in Fig. 146 corresponds to a separate place in the periodic table, and that two or more atoms occupying the same place are isotopes. For example, Ra B, Ra D, Ra G, are all isotopes of lead, with the same chemical properties, although, of course, the first two are radioactive and ordinary lead is not. (Indeed, native specimens of lead that have probably originated from the disintegration of uranium are found to have atomic

weights different from ordinary lead.) There are a great many radioactive isotopes. Thorium and actinium, like uranium, form disintegration series of their own; and many of the members of those two series are isotopes of members of the uranium series.

Periodic Group:											
III B	IV B	V B	VI B	VII B	0	I A	II A	III A	IV A	V A	VI A
81	82	83	84	85	Atomic 86	Number 87	88	89	90	91	92
Tl	Pb	Bi	Po		Element Rn		Ra		Th	Pa	U
	Ra G 206										
Ra C'' 210	Ra D 210	Ra E 210	Ra F 210								
	Ra B 214	Ra C 214	Ra C' 214								
			Ra A 218								
				Rn 222							
							Ra 226				
									Io 230		
										UX ₁ 234	
											UII 234
											UI 238

FIG. 146. *The Uranium Series in the Periodic Table*

Radium. This element has been of great interest because of its remarkable radioactive properties, and also because it is effective in the treatment of certain kinds of cancer. It belongs in the same family with barium and resembles that element in many of its properties.

Radium occurs only in uranium minerals, and practically all our supply comes from *pitchblende* (U_3O_8). Only 1 g of radium is present in 3.88 tons of the purest pitchblende — and this itself is a very rare mineral. Since the ores used are never pure, the yield of radium per ton is actually much less than that noted above.

For some years the United States was the largest producer of radium. In 1922 rich deposits of pitchblende found in the Belgian Congo enabled Belgium to become almost the sole producer. In recent years large deposits of the ore have been found in Canada, with the result that Canada promises to lead Belgium in the pro-

duction of radium and to supply all our needs at a reasonable cost. At present practically the entire output of the element comes from these two countries and amounts to about 100 g annually.

The cost of producing the pure element would make its use prohibitive. Fortunately its salts are as effective for our purposes as the element itself. The salts commonly used are the bromide (RaBr_2) and the sulfate (RaSO_4). The price of radium has been as high as \$150,000 per gram, but today it is normally \$40,000, although it has sold as low as \$25,000. This decline in price has been due not only to the discovery of richer deposits of pitchblende, but even more to the invention of X-ray tubes that produce rays as effective for medicinal purposes as those given off by radium, and at a much lower cost.

The largest use of radium is in the treatment of disease, notably of cancer, and the large hospitals are supplied with small amounts. It is kept in lead "bombs," the walls of which are about 4 in. thick to prevent the dangerous rays from passing through the metal. It is the very penetrating gamma rays that are the effective agent in this use. Often, instead of using radium itself, the gas radon, given off by radium, is collected and sealed into small, thin-walled glass ampules. These are then used in the treatment of cancer. There is a growing tendency, however, to use X rays from extremely high-voltage tubes for this treatment.

In the industries minute quantities of a mixture of radium compounds and mesothorium (an isotope of radium) are worked into varnishes and enamels and applied to watch hands, electric push buttons, door numbers, and similar small objects, to render them visible in the dark.

Radioactivity and the structure of the atom. In Chapter 3 the flashes in the spinthariscopes were offered as convincing evidence for the existence of particles of matter. In radioactive changes we have atoms going to pieces before our very eyes, so that we are forced to discard the old theory that atoms are simple homogeneous particles, and are compelled to think of them as complex systems, made up of smaller parts possibly arranged in some pattern or structure. The flying pieces from the exploding atom may be caught and manipulated in a magnetic or electrostatic field, and the bullet-like alpha particles and electrons directed against targets, fluorescent screens, and photographic plates. Such methods of studying these and other component particles of the atoms have been important in the development of our present picture, or theory, of the inner structure of the atom. This subject we shall explore in the following chapter.

Questions

1. (a) Explain what is meant by a "periodic" process. Mention (b) six periodic processes in nature; (c) one in mechanics or machinery.
2. State the periodic law and point out its defects. What are the relative merits of the Mendeléeff and Thomsen forms of the periodic table?
3. How are the atomic numbers of the elements determined?
4. Construct the periodic table from memory as far as the element of atomic number 20.
5. What is the meaning of the following terms as applied to the periodic table: *group, family, long period, short period*?
6. Enumerate the practical advantages of the periodic table as a classification of the elements. Give illustrations.
7. (a) What are isotopes? (b) How are the masses of the isotopes found experimentally? (c) On what basis may the fractional atomic weights of most of the elements be explained?
8. (a) How many isotopes of hydrogen are there? (b) of oxygen (see the table of isotopes in the Appendix)? (c) How many different water molecules are possible? (d) What is the molecular weight of each?
9. (a) What is the nature of the rays emitted during radioactive disintegration? (b) How may these three rays be detected and distinguished?
10. What general ideas about the structure of atoms result from a study of radioactivity?

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CHAPTER 14

The Structure of the Atom

Introduction. During nearly all the nineteenth century, chemists and physicists were content to look upon the atoms as hard, elastic, round, dense, unchanging particles. Not until about 1900 was it clearly realized that the characteristic properties and behaviors of atoms must mean that various species possess characteristic structures which determine their properties. Since even the largest atoms are about a thousand times too small to be seen in the most powerful microscope, we must give up all hope of direct observation and resort to inference and deduction in our attempts to understand the manner in which an atom is put together. The picture we get in this way, and which we agree to imagine as portraying the internal structure of the atom, we call a *theory of atomic structure*.

Illustration. If a very clever man, like Benjamin Franklin, could have seen an automobile of today, it is quite possible that he might have been able to make a fairly successful, reasoned deduction as to what its inner mechanism was, without even looking under the hood of the engine. Guided by the nature of the sounds coming from under the hood, the turning of the wheels, the vapors from the exhaust, and so on, he would try to imagine what kind of internal structure could produce the behavior characteristic of an automobile. This is essentially the sort of game that modern physicists and chemists are playing with the atom.

The structure of the atom. Working out the structure of the atom has been one of the most absorbing problems of physics and chemistry during the present century. The task is by no means completed, and our present theory is constantly shifting and growing. However, the experimental facts of atomic behavior remain facts, and the general truth of the modern concepts of atomic structure seems certain. We shall first present the facts about the various aspects of our problem and then decide what inferences may be drawn from the facts.

First, we should identify and characterize the unit parts out of which atoms are built, and then discuss the theory of how these parts are arranged in the various kinds of atoms.

The components of the atom. The evidence for the existence and nature of the several components that together make up the various

atoms has been gathered largely by physical rather than chemical methods. However, it is possible in a textbook of chemistry to describe in a general way the results achieved by the physicists. It seems that there are at least five component particles out of which atoms are built, as indicated in the following table :

NAME	CHARGE	MASS (O = 16)
The proton (p)	Positive by 1 unit	Large, 1.008
The neutron (n)	No charge	Large, 1.0084
The electron (e^-)	Negative by 1 unit	Very small, 0.000546
The positron (e^+)	Positive by 1 unit	Very small, 0.000546
The alpha particle (α)	Positive by 2 units	Very large, 4.003

1. *The electron.* About 1900 Sir Joseph Thomson (Fig. 147), as a result of his extensive study of the discharge of electricity through gases, succeeded in isolating tiny electric particles and in proving that they could be obtained from the various atoms. These particles are negative electrically and are called *electrons*. By manipulating the electron in electric and magnetic fields, Thomson was able to measure the *ratio* of the *charge* on the electron to the *mass* of the electron. By further work Millikan (Fig. 148) collected the necessary data for calculating the *charge* on the electron. This was accomplished by studying the behavior of charged oil drops (that is, drops which had lost or acquired one or more electrons) suspended between charged plates. These experiments showed that the charge on an oil drop was always equal to, or some whole multiple of, a definite unit charge, 4.80×10^{-10} electrostatic units. Other methods lead to substantially the same result. Simple calculation gives the mass of the electron as $\frac{1}{1838}$ that of the hydrogen atom. The electron, then, is a particle of negative *electricity* of definite charge and mass which is a universal constituent of matter and which in suitable multiples makes up all negative charges.

2. *The proton.* Naturally physicists searched for a *positively* charged particle corresponding to the electron in mass and charge. However, when the positive particle was isolated, it proved to be equal to the electron in charge, but in mass nearly equal to the hydrogen atom, namely to $\frac{1837}{1838}$ of that weight. This positive unit was called the *proton*. A proton plus an electron constitutes a hydrogen atom, and the proton itself is the hydrogen ion, H^+ .

3. *The neutron.* In more recent years a third atomic component has been discovered, called the *neutron*. As the name indicates, the



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FIG. 147. *Sir Joseph Thomson*
(1856-1940)

Formerly director of the Cavendish
Laboratory, Cambridge, England



FIG. 148. *Robert Andrews Millikan*
(1868-)

Director of the Physical Laboratory,
California Institute of Technology

neutron is electrically neutral, and its mass is almost equal to that of the hydrogen atom. As we shall see, neutrons are obtained by the disintegration of many types of atoms.

4. *The positron.* Much more recently it has been found that during atomic disintegration there is unmistakable evidence of the appearance of charges of positive electricity corresponding to the positive electron, which physicists hoped to find. Apparently these particles have a mass approximately equal to that of the electron, and a charge equal to that of the electron but of opposite sign. They are called *positrons* and appear only during atomic disintegration.

5. *The alpha particle.* Already (Chap. 13) we have seen that alpha particles are ejected from certain atoms undergoing radioactive disintegration. An alpha particle is an ion of helium (He^{++}); it carries 2 positive charges, and its mass is the same as that of a helium atom (minus the mass of 2 electrons). It is probably made of 2 protons and 2 neutrons, and such a constitution explains its charge of 2 and mass of 4.

Rough plan of atomic structure. We are now ready to describe the way in which these several particles are arranged in an atom. Before we approach the details, let us attempt to get a simple but

general idea of what an atom is like. We may say at once that an atom bears a striking formal resemblance to certain kinds of nuts, in the sense that both atoms and nuts possess kernels and shells (Fig. 149). In an atom the shell is inhabited only by electrons, which circulate through this outer region and give bulk and size to the atom. The other particles are in the kernel, or *nucleus*.

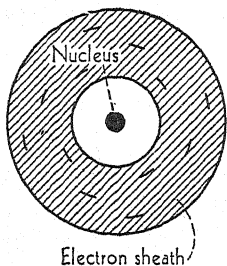


FIG. 149. *Diagram Showing Approximate Plan of Atomic Structure*

Of course to answer the question of how the component particles are arranged in an atom we must resort, as we have already said, to experimentation and deduction. All that we have to guide us is the characteristic behavior of the different atoms. There are various types of behavior which we may consider, but we shall select only a few of the more significant ones which bear directly on the problem. In our

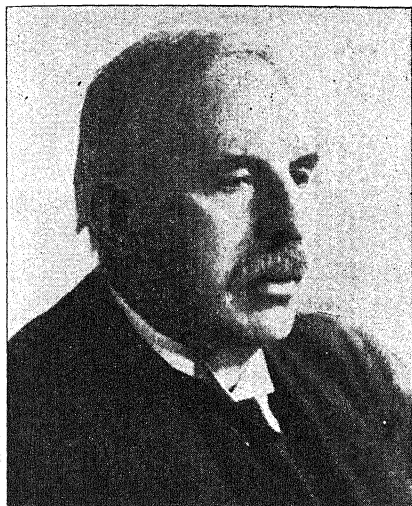
study of the nucleus, to be discussed first, let us now consider the following items at some length: (1) the behavior of atoms bombarded with alpha particles, (2) the behavior of atoms bombarded with electrons, (3) the existence of isotopes, (4) radioactivity.

THE NUCLEUS

1. Bombardment with Alpha Particles

Rutherford's experiments. With the recognition that electrons constitute an integral part of all atoms (Sir Joseph Thomson), one immediately feels that there must also be present in these atoms a positively charged portion, since atoms are normally neutral. This problem was solved by some experiments of Lord Rutherford.

Suppose that we were shooting at a target of rather large area with a machine gun, and that we scattered the fire all over the target. If now we were to introduce a pile of small cannon balls, the size of large oranges, and piled together as in Fig. 93 or Fig. 100 (pp. 130, 134), in front of the target and in the line of fire, certainly no bullets would be able to penetrate the pile and hit the target. They would bounce off the cannon balls. Rutherford (Fig. 150) performed essentially this same experiment with atoms. He directed a stream of atom bullets (*alpha particles*) at a fluorescent screen, so that the spots where the alpha particles struck the target could be observed (Fig. 152). Then he introduced into the line of fire, in front of the target, a piece of exceedingly thin gold foil, the atoms of which are piled together compactly, just as the cannon balls are in the face-centered cubic



Ramsey and Muspratt

FIG. 150. Lord Rutherford (1871-1937)

Director of the Cavendish Laboratory,
Cambridge, England



Science Service

FIG. 151. Niels Bohr (1885-)

Professor of theoretical physics, University of Copenhagen, and author of the Bohr theory

piling (Figs. 93, 100). In Rutherford's experiment most of the alpha particles went through the gold foil, which was at least several hundred atoms thick. However, some of the alpha particles were deflected from a straight path and were caused to veer off at sharp angles, and occasionally (few in many thousand) were repelled backward. Similar results were obtained with other metals.

Characteristics of the nucleus. The results of these alpha-particle experiments suggested to Rutherford that the gold atoms are not hard, solid spheres but are extremely open and porous in their structure. The alpha particles, traveling with terrific velocity, go directly through the atoms themselves, perhaps with the same relative ease with which the machine-gun bullets would cut through a pile of oranges instead of cannon balls. The only satisfactory suggestion which Rutherford could make to explain the deflection and repulsion of alpha particles was to suppose that *practically all the mass of the gold and other atoms is con-*

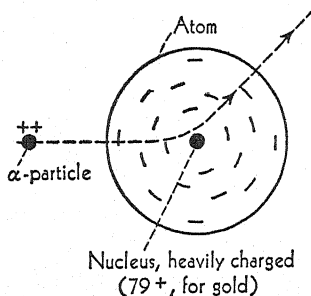


FIG. 152. Diagram Showing an Alpha Particle Passing through a Gold Atom

centrated at the center of the atom in a positively charged nucleus. The strong positive charge of the nucleus deflects or repels any of the positively charged alpha particles which in their flight through the metal atoms happen to pass close by a nucleus. The nucleus is hard and dense and is excessively small (diameter about 10^{-12} cm) compared with the whole atom (diameter about 10^{-8} cm). The electrons patrol the outer domain of the atom and guard it against invasion by other atoms.

From Rutherford's study of the exact angles of deflection of those alpha particles which were caused to deviate from a straight line, he was able to calculate, with fair accuracy, the actual charge on the nucleus of the gold atom (and other atoms). More accurate determination of the number of positive charges on the nucleus results from the Moseley method, as described below.

2. Bombardment with Electrons

Moseley's experiments and the charge on the nucleus. We have already described Moseley's experiments (p. 207) with an X-ray tube, in which the target is bombarded by electrons shot out from the cathode. The target may be made of any one of various elements or their compounds. The atoms in the surface of the target are subjected to the electron bombardment, and under this bombardment the atoms emit X rays.

In all atoms (except hydrogen) there are two electrons which inhabit a portion of the hull lying *very close* to the kernel (as we shall see later). It is the disturbance of these two electrons by the bombarding bullet electrons which results in the emission of X rays. When the nucleus of the atom carries a large positive charge, these two electrons are bound very tightly to it, and the X-ray wave length is short; in other atoms, of smaller nuclear charge, the binding is not so tight, and a longer wave is given out. Thus, the very fact that the X-ray wave lengths *decrease* regularly in stepwise fashion as we go up the atomic-number series means that the nuclear charges also *increase* regularly in a stepwise fashion, 2, 3, 4, 5, . . . , 92. *The number of positive charges on the nucleus of an atom is the same as the atomic number of the atom.*

Tentative theory of nuclear structure. Any theory of the structure of the nucleus of the atom must account not only for the positive electric charge on the nucleus but also for the mass of the atom, since this is almost entirely concentrated in the nucleus. It is rea-

sonable to suppose that the charge is due to protons. However, protons alone will not account for the mass of the atom, which (except in the case of the hydrogen atom) is two or more times as large as the number of positive charges. Now neutrons (mass, approximately 1) contribute mass without adding to the charge, so that we may add to the number of the protons present in the nucleus of the atom a sufficient number of neutrons to furnish the requisite mass, as shown below for the first ten elements in the periodic table, in which protons and neutrons are designated by the letters p and n respectively.

	H	He	Li	Be	B	C	N	O	F	Ne
	$\begin{pmatrix} 1p \\ 0n \end{pmatrix}$	$\begin{pmatrix} 2p \\ 2n \end{pmatrix}$	$\begin{pmatrix} 3p \\ 4n \end{pmatrix}$	$\begin{pmatrix} 4p \\ 5n \end{pmatrix}$	$\begin{pmatrix} 5p \\ 6n \end{pmatrix}$	$\begin{pmatrix} 6p \\ 6n \end{pmatrix}$	$\begin{pmatrix} 7p \\ 7n \end{pmatrix}$	$\begin{pmatrix} 8p \\ 8n \end{pmatrix}$	$\begin{pmatrix} 9p \\ 10n \end{pmatrix}$	$\begin{pmatrix} 10p \\ 10n \end{pmatrix}$
Charges on nucleus:	1+	2+	3+	4+	5+	6+	7+	8+	9+	10+
Resulting atomic mass:	1	4	7	9	11	12	14	16	19	20

FIG. 153. *Nuclei of the First Ten Atoms*

Our picture accounts not only for atomic numbers (number of positive charges) but also approximately for atomic weights. It is in line with the results of Rutherford's experiments, which show that most of an atom's mass is concentrated in the nucleus, for we have placed the two massive components of the atoms, the protons and neutrons, in the nucleus. Indeed, this tentative theory is already very close to the truth; and with a few further modifications, which we shall want to make as we consider isotopes and radioactivity, we may say that it represents substantially the views of modern physicists about the composition of atomic nuclei.

3. Isotopes

Nuclei of isotopes. In the previous chapter we saw that *isotopes* are atoms having the same atomic number and chemical characteristics but different atomic masses, and that it is in terms of *mixtures of isotopes* that we account for fractional atomic weights. How do the atomic nuclei of the isotopes differ from one another?

To answer this question, let us take the case of lithium. It has been demonstrated experimentally (positive rays) that some lithium

atoms have an atomic weight of 6 and others of 7. If we took a lithium atom of atomic weight 6, with a nucleus of the composition shown in Fig. 154, *A*, and introduced into the nucleus another neutron (Fig. 154, *B*), we should

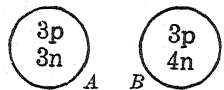


FIG. 154. *Nuclei of Isotopes of Lithium*

increase the atomic weight to 7 without disturbing the nuclear charge (which is 3 + in each case). Neutrons would not change the arrangement of the electrons in the outer regions (hull) of the atom, which, as we shall see (p. 240), determines the *chemical properties* of the atom. The three chlorine isotopes would have nuclei of the compositions shown in Fig. 155, *A*, *B*, and *C*), and similarly for isotopes of other elements.

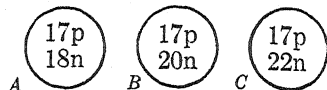


FIG. 155. *Nuclei of Isotopes of Chlorine*

4. Radioactivity

Alpha particles in the nucleus. It seems reasonable to suppose that alpha particles are present in the nuclei of all atoms (except hydrogen). They are shot off from the nuclei of some atoms during radioactive disintegration; and while the nuclei of some light atoms can be disintegrated by alpha-particle bombardment (as we shall see later in this chapter), it is true that atoms like carbon, oxygen, and silicon, having atomic weights which are *multiples of the weight of the alpha particle* (4), *cannot* be disintegrated in this way.

So far, in the preceding few pages, we have represented the nucleus as being made up of protons and neutrons. But, since modern theory suggests that an alpha particle be substituted for every set of two protons and two neutrons (2 *p*, 2 *n*), we may now show the following nuclear compositions for the first ten atoms:

	H	He	Li	Be	B	C	N	O	F	Ne
Charges on nucleus:	1 +	2 +	3 +	4 +	5 +	6 +	7 +	8 +	9 +	10 +
Resulting atomic mass:	1	4	7	9	11	12	14	16	19	20

FIG. 156. *Atomic Nuclei in Terms of Alpha Particles*

Since an alpha particle has a charge of 2 + and a mass of 4, it will be observed that the atomic number and atomic weight are properly accounted for in every case. Similarly the composition of all other atomic nuclei may be set down in terms of α , *p*, *n*.

Changes in the nucleus and the periodic table. We may now explain the shifting position, in the periodic table, of the members of the uranium series, described in the last chapter. The compositions of the nuclei of U I, U X₁, U X₂, and U II are shown in Fig. 157. When the nucleus of U I (nuclear charge 92 +) loses an alpha particle, it loses a charge of 2 + and a mass of 4. Therefore the atomic number of U X₁ will be reduced to 90, and the atom U X₁ will be shifted over *two* places toward the left in the periodic table. At the same time its atomic weight is cut to 234. The parent U I and the offspring U X₁ are thus, of course, two different elements with different physical and chemical properties. Then, when U X₁ loses a beta particle (an electron *negatively* charged) from its nucleus to form U X₂, the nuclear charge will increase to 91 +, and there will be a shift of one place to the *right* in the table. The electron may possibly be present as such in the nucleus, or it may come from a neutron, which then changes into a proton (as shown in the figure). The atomic weight will remain exactly the same, except for the weight of the escaped electron.

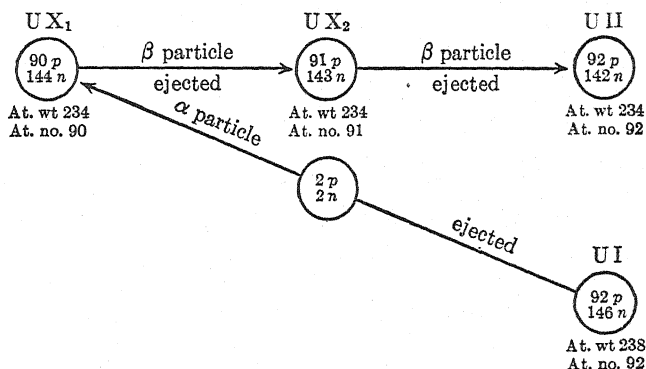


FIG. 157. *The Disintegration of Uranium I into Uranium II*

U II, formed from U X₂ by the loss of a beta particle, will have a nuclear charge of 92 +, that is, the same atomic number as U I. In fact, these two atoms, U I and U II, one of atomic weight 238, the other 234, are isotopes occupying the same place in the periodic table.

THE ELECTRONS OF THE ATOM

Evidence for the distribution of the electrons. Let us now turn our attention to the arrangement of the electrons which circulate in

the outer region of the atom. We may discuss three lines of evidence which are helpful in forming a theory about the positions of the electrons: (1) spectroscopic behavior, (2) periodic-table behavior, and (3) chemical combination.

1. Spectroscopic Behavior

The spectrum of the hydrogen atom. In Chapter 9 we described the spectroscope and several types of spectra. Let us consider the spectrum of the hydrogen atom. If hydrogen gas is introduced, at low pressure, into a Plücker tube (Fig. 106, p. 146) and excited by the electric discharge from an induction coil, some of the molecules are split up into atoms; and these atoms glow, or give out light, which may be examined spectroscopically. The spectrum is not continuous, but is a series of colored lines, of the type shown in the color plate facing page 145. The first line is red, the second blue, the third violet, the fourth very close to the ultraviolet, and the rest, getting closer together, are in the ultraviolet region.

The Bohr theory. We have very good reasons for believing that the single electron, in the space surrounding the nucleus of the hydrogen atom, is responsible for the production of these spectral lines. According to the theory suggested by the Dane Niels Bohr (Fig. 151), the hydrogen atom is something like a solar system, with the electron revolving around the nucleus. The electron is supposed to be able to move in a number of different orbits, or in different energy levels, as shown in Fig. 158 — *K, L, M, N, O*. Bohr supposed that the electron can revolve only in these fixed orbits, and *not* in other orbits between them, as though the orbits were fixed tracks in space. In the usual hydrogen atom, in its normal state, the electron is in the *K* level. But the hydrogen atom can be made to absorb energy, under electron bombardment in the Plücker tube or by illumination with light of a suitable sort, and the electron can thus be lifted to a higher level, *L, M, N*, etc.; or it can be lifted entirely out of the atom, in which case the atom becomes ionized (H^+). As soon as the excitation of the atom ceases, the electron starts to fall back again from the higher energy levels to the lower energy levels, that is, from the outer to the inner levels. The energy released by these falls is emitted by the atom as light; and the greater the energy of fall, the shorter the wave length of the light, as shown in the atom diagram in Fig. 158.

The situation reminds us of an elevator, if we suppose that by automatic control the elevator car can stop only at the floor levels, not between floors.

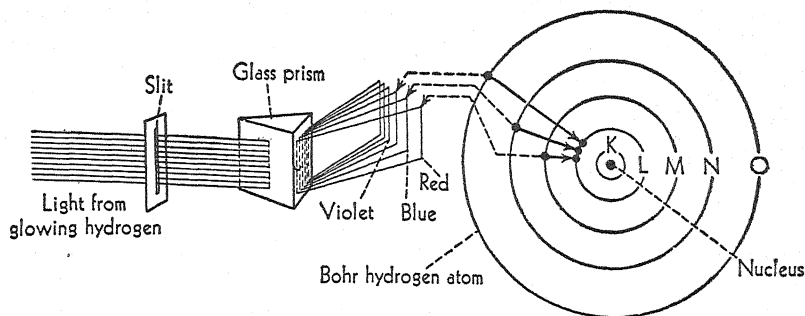
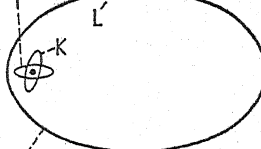


FIG. 158. *Diagram Showing the Relation between the Wave Lengths of Light and the Falls of the Electron in the Hydrogen Atoms, as Interpreted by the Bohr Theory*

The elevator, normally waiting for passengers on the ground level, can by the absorption of energy be lifted to any floor above; then, when it falls back to lower floors, energy is released — the greater the fall, the greater the energy released.

Atoms of atomic number greater than 1 evidently contain more than one electron, and, in the Bohr theory, each of these electrons circulates in orbits. There may be more than *one* orbit in a given energy level, or shell. The K shell will hold no more than *two* electrons (in two orbits). The L shell will hold as many as *eight*, and the M shell *eighteen*. It should be said that the orbits, for the most part, are elliptical rather than circular. The Bohr orbit-diagrams for several of these more complicated atoms — lithium, sodium, and argon — are shown in Figs. 159, 160, and 161.

2 electrons in orbits in K shell,
which will accommodate
no more than 2 electrons



1 electron in orbit in L shell

FIG. 159. *Bohr Diagram of Lithium Atom*

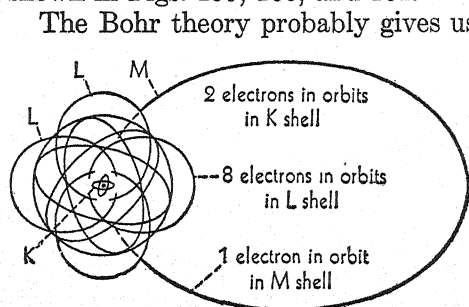


FIG. 160. *Bohr Diagram of Sodium Atom*

The Bohr theory probably gives us the best picture of the outer region of the atom that we shall ever have, and that is why some attention has been devoted to it here. It has now been displaced by the "wave-mechanics" theory, according to which the electrons circulate in the atom like waves rather than like particles. The new theory is

extremely satisfactory, but it is highly mathematical and is not easy to grasp. For many purposes the more pictorial Bohr theory yields virtually the same results in a qualitative way. The *energy levels*, or *shells*, in which we shall now be chiefly interested, are retained in the new theory.

Quantum theory. We have good reasons for believing that energy, like matter, is not continuous but is made up of pieces. This is the quantum theory of energy structure. The energy carried by a ray of light travels in little bunches, or *quanta*. The magnitude of the energy in a quantum is directly proportional to the frequency of the light, or, in mathematical symbols,

$$E = h\nu$$

where E is the energy of a quantum, h is a proportionality constant (known as the Planck constant), and ν is the frequency, or the number of waves passing a point in a unit of time. Since wave length is inversely proportional to frequency, it follows that the quanta of long waves, like radio waves, carry very little energy, and that the quanta get larger and larger as we proceed to shorter and shorter waves through the whole known spectrum of frequencies, through heat waves, the infrared, the visible, the ultraviolet, to X rays, gamma rays, and finally to the cosmic rays, which have the shortest wave length, the greatest frequency, and the largest quanta.

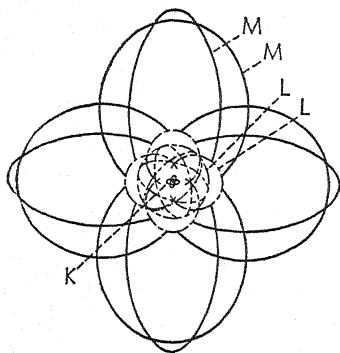


FIG. 161. Bohr Diagram of Argon Atom

For example, in the Bohr hydrogen atom (Fig. 158) the electron in the K level, when it is exposed to an inflow of energy, is not lifted out of its position at all, until and unless the quantum of energy which it receives is big enough to lift it all the way, say to the L level or the M level. All the energy transfers which occur between light rays, electrons, atoms, and molecules are in quanta, a discontinuous, particle-of-energy exchange. When we are working with large quantities of energy involving a huge number of quanta, the small-piece structure of the energy is apparently obliterated, or smoothed out.

2. Periodic-Table Behavior

Periodic arrangement of electrons. From the periodic table of the previous chapter let us take the nineteen elements beginning with helium.

He	Li	Be	B	C	N	O	F
Ne	Na	Mg	Al	Si	P	S	Cl
A	K	Ca	etc.				

The atoms in the vertical columns, above and below one another, are alike. This periodicity cannot be due to the nuclear charge (atomic number), which increases *regularly* in steps as we go from the lightest to the heaviest atom. It therefore must be a function of some recurrent periodicity in the arrangement of the electrons.

We know that the helium atom is a very stable arrangement of nucleus and 2 electrons (in the *K* shell). Therefore, when we find that an atom of lithium, which possesses 3 electrons, very readily loses one of them to form a lithium ion (Li^+), we must let this behavior of the third electron, entirely different from the other two, be reflected in an entirely different type of electron arrangement. So we suppose that this electron is placed in the next outer shell, the *L* shell (see Bohr diagram, Fig. 159), where it is not held nearly so tightly by the nucleus as the other 2 electrons, deeper down in the *K* shell. Beryllium, the next atom in the series, has a total of 4 electrons, 2 of which are very easily removed to form the beryllium ion (Be^{++}); and correspondingly these 2 electrons are in the *L* shell. Similarly, as we continue up the series, increasing the nuclear charge a step at a time, the atoms B, C, N, O, F, will have respectively 3, 4, 5, 6, 7 electrons in orbits in the *L* shell. Finally we come to neon, which has 8 *L* electrons. It happens that an outer shell of 8 electrons is very symmetrical and very stable, and shows very little tendency to part with any of its electrons or to take on any new electrons in its shell (*L* shell). Neon thus resembles helium in its stability, and in fact in many of its other properties.

When we come to the element sodium, with 9 electrons (not counting the 2 *K*-shell electrons, which are found close to the nucleus in the *K* shell in *all* the atoms of the periodic table), we again observe a great readiness to lose *one* electron. Consequently, to indicate this difference from the behavior of the other 8 electrons in the *L* shell, we represent the sodium atom (compare Fig. 160) with 1 outer electron in the *M* shell. Proceeding through the series of atoms in the second row, we fill up the *M* shell step by step, until we come to argon (Fig. 161), where again the outer shell contains 8 electron orbits and is very stable. Potassium, the next atom, will have a single electron in the *N* shell, and will of course resemble sodium and lithium, not only in the ease with which it ionizes (K^+) but also in its spectroscopic and other types of behavior. From these few illustra-

tions the student will readily grasp the idea and see that from a consideration of periodic-table behavior we can set up a theory of the arrangement of the electrons to account for the periodic recurrence of resemblances among the atoms.

Distribution of the electrons among the various levels. The question naturally arises in the case of those elements which possess a considerable number of electrons, How are these distributed among the various levels or shells? Space forbids giving the distribution of the electrons for all the elements, but it may be of interest to give it for the rare-gas elements. This is as follows:

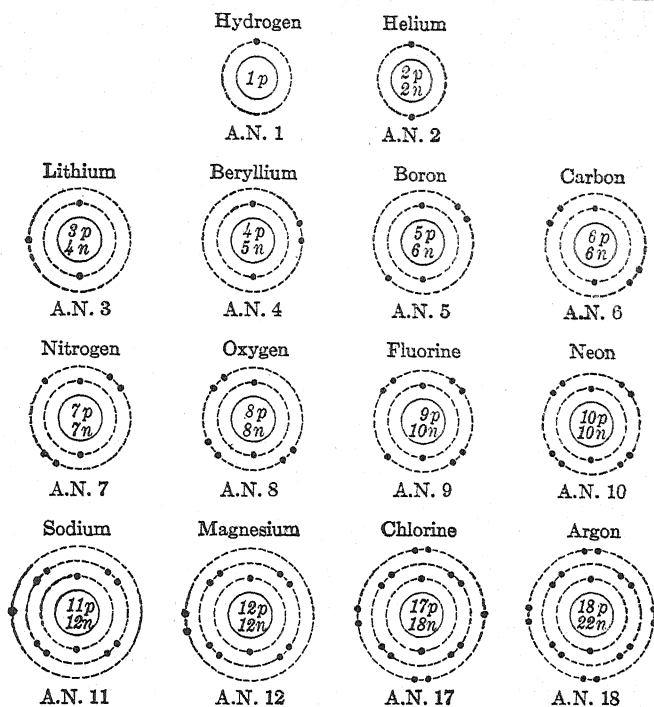
	<i>K</i>	<i>L</i>	<i>M</i>	<i>N</i>	<i>O</i>	<i>P</i>
He	2	—	—	—	—	—
Ne	2	8	—	—	—	—
Ar	2	8	8	—	—	—
Kr	2	8	18	8	—	—
Xe	2	8	18	18	8	—
Rn	2	8	18	32	18	8

3. Chemical Combination

The chemist and atomic structure. While all that we have just said about the structure of atoms is interesting and important, we have as yet said very little about the question which is of primary concern to chemists: Why do atoms combine with one another?

A simplified representation of atomic structure. To help us in our symbolic representation of the atoms in chemical combination, let us adopt the simplified and convenient scheme shown in Fig. 162. The dotted circles do *not* represent orbits, but the energy levels, or shells, *K*, *L*, *M*, etc. In these shells we put the various numbers of electrons which a consideration of spectroscopic behavior and of periodic-table behavior has shown to be there.

The driving forces in chemical combination. Atoms are held together, of course, by electrical forces. A most important factor, involving the manner in which these attractive forces can come into play, is *symmetry*. We know that the rare-gas atoms are extremely *inert* chemically and form no stable compounds. We also know that their outer shells hold 8 electrons (2 in case of He), and we feel sure that their chemical inertness is caused by the symmetry and stability of their outer electron shell (Fig. 161). *All other atoms tend strongly to reach the stable electron configuration of the rare-gas atoms by processes of gaining or losing electrons, and it is this tendency which results in the chemical combination of atoms.*

FIG. 162. *Simplified Representation of the Atoms Indicated*

In the inner circle the nuclear composition is given. The first circle outside the nucleus represents the *K* shell, the second one the *L* shell, and the third one the *M* shell. In the case of isotopic elements, the nuclear composition of the most abundant isotope is given.

There are two distinct ways in which the electrons of the *outer shells* of two or more atoms may be redistributed during chemical action, resulting in two distinct types of compounds. These are called (1) electrovalent compounds and (2) covalent compounds.

1. **Electrovalent compounds.** Let us consider a sodium atom (see Fig. 162), which we may think of as saying to itself: "Well, look at my neighbor there, the neon atom. Its outer shell has its full quota of electrons — none lacking, none left over. It is so independent and forms no compounds because it has its 8 electrons symmetrically arranged. If I could only get rid of this one extra electron of mine, I too should have the independent symmetry of neon." Obviously this is highly figurative language. Nevertheless the sodium atom and indeed *all* the atoms act exactly in this way, as though striving to get 8 electrons in their outermost shell of electrons and so resemble the inert gas nearest them.

Accordingly, when a sodium atom meets a fluorine atom, the sodium atom is exceedingly anxious to get rid of its single outer electron, and the fluorine atom

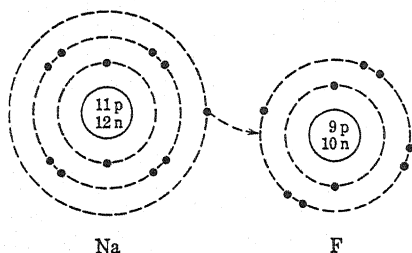


FIG. 163. *The Combination of Sodium and Fluorine to Form Sodium Fluoride*

(with 7 outer electrons) is equally anxious to add an eighth electron. As a result, the electron transfer actually occurs as represented in Fig. 163. After giving up its electron, the neutral sodium atom is, of course, positively charged; and the fluorine atom, accepting the electron, acquires a negative charge. In chemical symbols we may represent the

exchange thus: $\text{Na} + \text{F} \longrightarrow \text{Na}^+ + \text{F}^-$. The two species of charged atoms (*ions*) are then attracted by electrostatic forces. Electrovalent compounds and, in general, most inorganic compounds are simply clusters of oppositely charged ions, formed by the surrender and gain of one or more electrons between atoms, and held together in definite ratios by electrostatic forces.

Examples. Sodium will also lose its electron to chlorine: $\text{Na} + \text{Cl} \longrightarrow \text{Na}^+ + \text{Cl}^-$; as will also potassium, which reverts to the *argon* shell: $\text{K} + \text{Cl} \longrightarrow \text{K}^+ + \text{Cl}^-$. Lithium, which envies the symmetry of its close neighbor helium, will also lend its electron to chlorine or fluorine: $\text{Li} + \text{Cl} \longrightarrow \text{Li}^+ + \text{Cl}^-$. When sodium reacts chemically with oxygen to form Na_2O , two atoms, each giving one electron, are necessary, since an oxygen atom needs *two* electrons to fill out its octet: $2\text{Na} + \text{O} \longrightarrow 2\text{Na}^+ + \text{O}^{--}$. But when Mg and Ca react with O to form MgO and CaO , a single atom of Mg and Ca will do, since each one carries *two* outer *M* electrons: $\text{Mg} + \text{O} \longrightarrow \text{Mg}^{++} + \text{O}^{--}$; and $\text{Ca} + \text{O} \longrightarrow \text{Ca}^{++} + \text{O}^{--}$. Aluminum will react with chlorine to form AlCl_3 , as follows: $\text{Al} + 3\text{Cl} \longrightarrow \text{Al}^{+++} + 3\text{Cl}^-$; and with oxygen, $2\text{Al} + 3\text{O} \longrightarrow 2\text{Al}^{+++} + 3\text{O}^{--}$, to give the compound Al_2O_3 .

2. Covalent compounds. In many cases, especially among *organic* compounds, and in the make-up of complex ions such as SO_4^{--} , the constituent atoms cannot reach the desired condition of 8 outer electrons by a process of give and take, because *both atoms have a deficit*. So they resort to a different plan. Each atom contributes an electron to form a *pair*, held in common by both atoms, and counting in the outer shell of each. This pair of shared electrons constitutes a single bond of the usual formula and is called a *covalent bond*.

Fig. 164 illustrates such a union between two fluorine atoms to make a fluorine molecule. Each atom had 7 outer electrons; by sharing a pair, each can claim 8. *Atoms held together by one or more pairs of shared electrons constitute covalent compounds.* The constituent atoms are closely bound into molecules, they are not oppositely charged, and they do not yield ions.

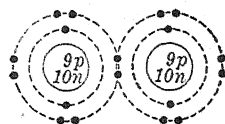


FIG. 164. The Fluorine Molecule (F_2)

Nitrogen will react with hydrogen to form ammonia (NH_3). Each hydrogen atom needs one more electron to make it similar to its neighboring inactive gas, helium; for the latter has but 2 electrons in its outer shell (Fig. 162). The nitrogen atom, with 5 electrons,

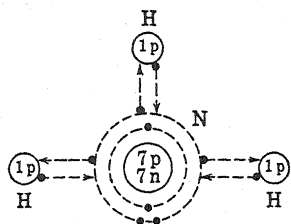


FIG. 165. The Diagram of Ammonia

needs 3 more to complete its number to 8. By agreeing to share pairs of electrons all four atoms can get what they want. The relations are indicated in Fig. 165. It will be noticed that in the molecule of ammonia the nitrogen atom still has a pair of unshared electrons, and it will be remembered that the hydrogen ion (H^+) has *no* electrons. Consequently, when a molecule of ammonia meets a hydrogen ion, they

share this lone pair of electrons belonging to nitrogen, and form the ammonium ion, NH_4^+ .

Carbon will react with chlorine to form a compound called carbon tetrachloride (CCl_4). Fig. 166 is a diagram that indicates the distribution of the electrons in this compound. It will be remembered that carbon has but 4 electrons in its outer shell, and that it needs 4 more for completion, while each chlorine atom has 7 and needs but 1 more. Each chlorine atom shares 1 of its electrons with 1 of those of carbon, and this process provides 4 pairs of shared electrons, constituting 4 covalent bonds.

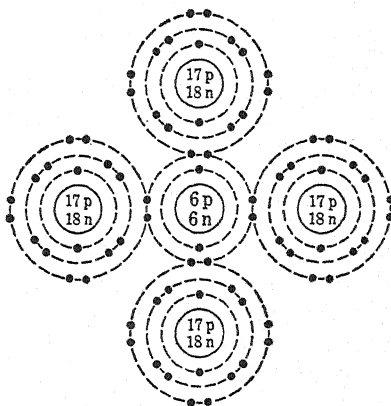


FIG. 166. The Diagram of Carbon Tetrachloride

Representation of covalent linking. It is inconvenient to draw such diagrams to show covalent linking. So it is customary to repre-

sent a pair of valence electrons by a colon (:). The fluorine atom is $\cdot\ddot{\text{F}}\cdot$; the fluorine molecule $\cdot\ddot{\text{F}}:\ddot{\text{F}}\cdot$; hydrogen chloride is $\text{H}:\ddot{\text{Cl}}\cdot$.

Electronic theory of valence. If we are right in assuming that chemical combination is due to the transfer of electrons from one

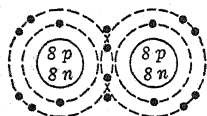


FIG. 167. *The Oxygen Molecule*

atom to another, or to the sharing of pairs of electrons by atoms, then *valence expresses the number of electrons transferred or the pairs shared*. An atom that takes up or loses 1 electron or shares a pair with another atom is a univalent atom. If it takes up or loses 2 electrons or shares 2 pairs, it is bivalent. In the oxygen molecule (Fig. 167) each oxygen atom shares 2 pairs of electrons with the other atom, and is bivalent. In carbon dioxide (Fig. 168) the carbon atom shares 4 pairs of electrons with 2 oxygen atoms. The carbon atom is therefore quadrivalent, each oxygen atom is bivalent, and the compound is covalent.

Valence electrons. It will be observed that only the electrons in the outer electron system (or shell) are concerned in chemical actions, and in determining the valence of an atom. The pair of *K* electrons, and those in inner completed shells, take no part in the action. For this reason the electrons in the outer incomplete shell are called *valence electrons*. The rare-gas atoms, with their outer shells already completed, have no valence electrons and are inert chemically (p. 142).

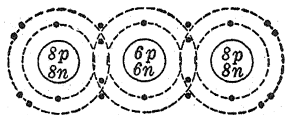
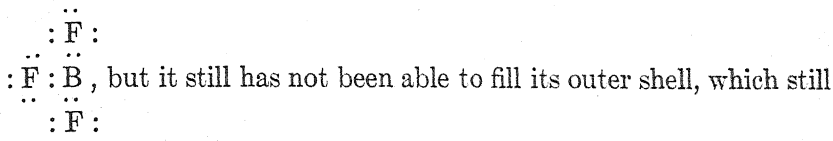


FIG. 168. *Diagram of Carbon Dioxide*

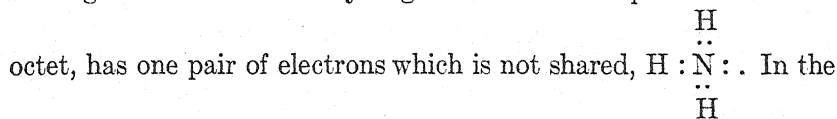
Positive and negative valences. In electrovalent compounds it is often desirable to specify whether the valence of an atom is due to the loss or to the gain of an electron. An atom that takes up one or more electrons, and so becomes electrically negative, is said to have *negative* valence; while an atom that loses one or more electrons, and thereby becomes electrically positive, is said to have *positive* valence. Thus in sodium fluoride (Fig. 163) the sodium has positive valence of 1 and the fluorine has negative valence of 1.

Valence of complex ions. Groups of atoms may form complex ions which have definite valences. In some cases, like the ammonium ion, NH_4^+ , they have positive valence. More often they have negative valence, as is the case with the nitrate ion, NO_3^- , and the sulfate ion, SO_4^{--} . The atoms within the ion are held together by predominantly covalent bonds.

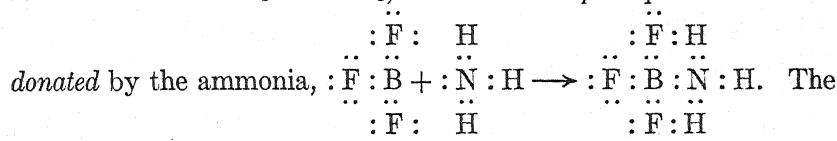
Co-ordinate covalence. Compounds which are at first troublesome to reconcile with the simple electronic picture of valence just outlined are those which are formed between apparently saturated molecules. Thus the two gases ammonia and boron trifluoride, BF_3 , combine readily. The boron atom has 3 electrons in its valence shell; it shares these with 1 electron from each of 3 fluorine atoms to form



lacks 2 electrons. The nitrogen of ammonia, on the other hand, in sharing electrons with 3 hydrogen atoms to complete its valence



reaction between BF_3 and NH_3 , the former *accepts* a pair of electrons



boron in BF_3 completes its octet without contributing any electrons of its own in the link with nitrogen.

This type of linkage involves a shared pair of electrons and in many cases is indistinguishable from the ordinary covalent bond. To distinguish it from a normal covalence, it is called a *co-ordinate covalence*. It is sometimes represented by an arrow, which indicates the origin of the shared pair, $\text{F}_3\text{B} \leftarrow \text{NH}_3$. We may summarize diagrammatically the types of valence linkage in the following manner:

1. Electrovalence $\text{A} \cdot + \cdot \text{B} \longrightarrow \text{A}^+ + : \text{B}^-$.
2. Covalence
 - a. Normal $\text{A} \cdot + \cdot \text{B} \longrightarrow \text{A} : \text{B}$ (or $\text{A} - \text{B}$)
 - b. Co-ordinate $\text{A} + : \text{B} \longrightarrow \text{A} : \text{B}$ (or $\text{A} \leftarrow \text{B}$)

NUCLEAR REACTIONS AND ARTIFICIAL RADIOACTIVITY

Nuclear reactions. Since atomic nuclei seem to be made up of particles (alpha particles, protons, and neutrons), the idea suggests itself that some of these particles could be knocked out of the nucleus by bombardment. Results equivalent to this have been accomplished in a great many cases. Bombarding particles get into the nucleus; then reactions occur inside the nucleus (resembling chemical reactions in some respects), and certain products are shot out from the nucleus. These novel nuclear reactions have fascinated many physicists and chemists during recent years.

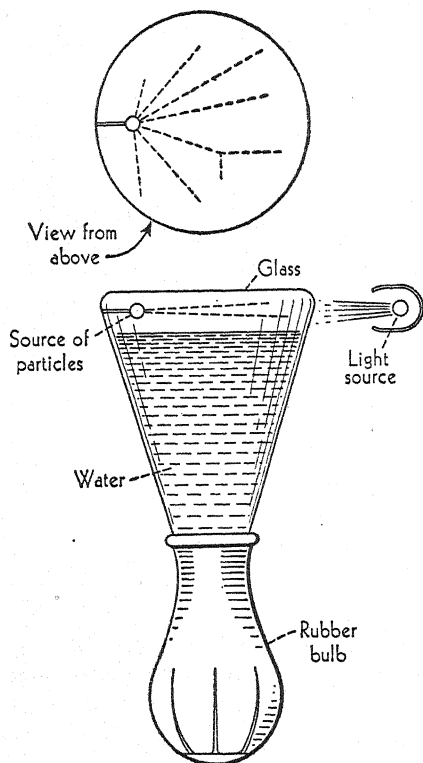


FIG. 169. *Simplified Cloud Chamber*

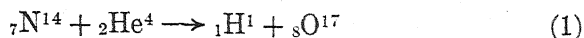
The bulb is compressed to force water up into the chamber and is then suddenly released. The expanding air or other gas is thus chilled and becomes supersaturated with water vapor

Water droplets condense on these ions, and thus render the track of the particle visible as a misty string of tiny water beads. The traces are photographed. From the character of the forks in these fog tracks, where nuclear disintegrations occur, the nature of the products of the disintegration can be inferred.

Bombardment with alpha particles. As atom bullets for shooting a nucleus, the alpha particles would seem to be ideal, since they

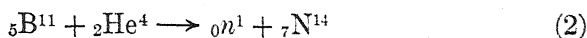
The cloud chamber. The course of nuclear reactions is followed by a study of the products formed by known reactants, just as with ordinary chemical reactions. But in nuclear reactions *individual particles* may be studied. One means for doing this is the Wilson cloud chamber (Fig. 169). The atom particles under examination, which of course are much too small to be seen, are allowed to travel in a gas space supersaturated with water vapor. The particles, along their path, collide with gas molecules and ionize thousands of them.

themselves are shot as projectiles out of the nuclei of some radioactive atoms at terrific velocities (9000 to 14,000 miles per second, p. 222). In the first authentic case of a nuclear reaction (observed by Rutherford) an alpha particle was buried in the nucleus of a nitrogen atom, a proton was ejected, and an oxygen atom (isotope of mass 17) was left as the residue :

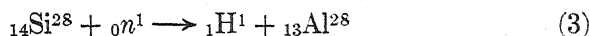


The number above the symbol indicates the atomic mass and the one below shows the atomic number. Only about 1 out of 10,000 alpha particles shot at nitrogen nuclei makes an effective collision.

Bombardment with neutrons. When the boron isotope of mass 11 is bombarded with alpha particles, *neutrons* (mass = 1, charge = 0) are emitted :

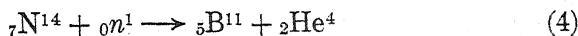


This reaction is a convenient source for neutrons, which, since they are without charge, are *not repelled* by a nucleus, and make excellent bullets. Any nucleus, no matter what its atomic number, can be invaded by a neutron, and even atoms of uranium have been disintegrated by neutrons. An interesting and typical example of a neutron reaction is the following :



The gain of a neutron and loss of a proton does not change the mass but reduces the atomic number from 14 to 13, and thus results in the transmutation of atoms of silicon into atoms of aluminum.

A reaction which is just the reverse of (2) above has been found to occur :



So it seems that there may be reversible reactions in a nucleus. Some nuclear reactions are endothermic and others exothermic, and usually enormous quantities of energy (per gram-atomic weight transformed) are involved. This is the origin of the speculation as to whether atomic energy may serve us in the future instead of our present fuel resources. But so far the fraction of effective impacts in bombardment of nuclei is extremely small.

The cyclotron. Other convenient bullets are hydrogen ions and heavy hydrogen ions, or protons (${}_1\text{H}^1$) and deuterons (${}_1\text{H}^2$), as they are often called. These particles are accelerated and brought up to high velocity by

different methods, one of the most effective of which is the cyclotron method.

The cyclotron is a large circular box, like a pillbox, made of brass, and cut in half, as shown (Fig. 170). The two sections, joined with an insulating material, are charged (one positively and the other negatively) to about 10,000 v potential difference. A powerful magnetic field is applied, with the lines of force running perpendicular to the paper in the figure.

A particle carrying positive charge (for instance, H^+), when introduced into the apparatus near the center, will first be repelled by A and attracted

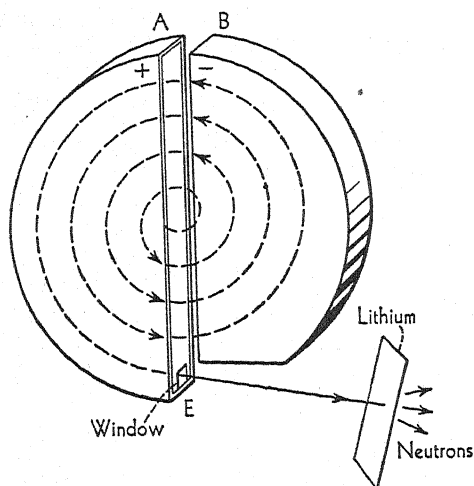
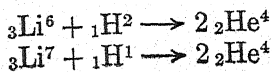


FIG. 170. *Diagram Illustrating Principle of Cyclotron*

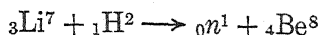
into section B; and as it moves, it will follow a curved path in the magnetic field, as shown in Fig. 138 and Fig. 145. The apparatus is so arranged that when the particle again reaches the gap between A and B, the electric field is reversed, and the particle is repelled by B and attracted by A. In this way the particle gathers speed repeatedly, and travels in an ever-widening spiral, until it issues at E with a velocity which in some cyclotrons may be as great as 25,000 miles per second. The cyclotron chamber is evacuated to eliminate collision with air molecules, and the exit E is a thin metal-foil window.

Enormous magnets are required. Some have been built weighing about 100 tons; and it is not unlikely that those planned for the future, to yield even greater velocities, will weigh thousands of tons. The larger and stronger the magnetic field, the more frequently can the spiraling particle be made to cross the gap.

Bombardment with protons and deuterons. The stream of high-speed protons or deuterons, out of the cyclotron, may be directed at nuclear targets of various elements and a great variety of transmutations achieved. For example, lithium atoms of mass 6 and 7, when bombarded, respectively, with deuterons and protons, give alpha particles in both cases:

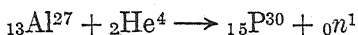


A rich source of neutrons (Fig. 170) is the reaction between deuterons and lithium (mass 7) :

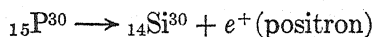


Artificial radioactivity. Certain nuclei, when bombarded, undergo a reaction which is not completed at once. They may slowly disintegrate in the manner of radioactive atoms, with a measurable half-life period. In this way, atoms of elements not normally radioactive may be made radioactive. In their decay all these artificial radioactive elements emit either electrons or positrons.

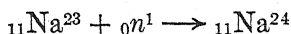
For example, aluminum bombarded with alpha particles yields radioactive phosphorus :



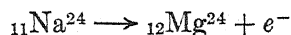
Then the phosphorus, with a half-life of 3 minutes, disintegrates into silicon :



Sodium bombarded with neutrons turns into radioactive sodium,



and this decays, with a half-life of 14.8 hours, to give magnesium



Radioactive sodium can be prepared in considerable quantity easily if a cyclotron is available, and it is possible that it may find a use as a substitute for radium (and radon) in cancer treatment.

Tracer reactions. Now that *light* atoms can be prepared in radioactive form, many significant studies can be made. For instance, the details of the metabolism of plants and animals are being followed in this way. How long a time is required for the calcium of food to reach the bones and be deposited in the bone tissue? The progress of radioactive calcium (half-life about 4 hours) through an animal's body can be followed with a sensitive electroscope. Sulfur and phosphorus metabolism are open to the same type of investigation. Radioactive phosphorus, ${}_{15}\text{P}^{30}$, has too short a half-life period (3 minutes) to be practical as a tracer, but another radioactive isotope, ${}_{15}\text{P}^{32}$, which has also been prepared, has a half-life of 14.5 days; and it has been used in studies of this sort. The whole field has immense future possibilities. These atoms are "tagged," and what they do and where they go can be observed.

Questions

1. Is there any good reason why what we now call a positive charge and a negative charge should not originally have been called, respectively, negative and positive? Explain.
2. Explain how it is possible for the nucleus of an atom to be many thousands of times more dense than the atom itself.
3. What is the composition of the nucleus of each of the following atoms: (a) titanium, at. no. 22, at. wt 48; (b) arsenic, at. no. 33, at. wt 75; (c) indium, at. no. 49, at. wt 115; (d) cesium, at. no. 55, at. wt 133.
4. What is the composition of the nuclei of the isotopes of (a) potassium (at. no. 19) having the mass numbers 39 and 41 and those of (b) strontium (at. no. 38) having the mass numbers 86, 87, and 88?
5. Draw a diagram showing the arrangement of electrons (a) for the atoms of calcium and oxygen; (b) for the ions of calcium and oxygen; (c) for the compound calcium oxide.
6. Draw a diagram showing the arrangement of electrons (a) for chloroform (CHCl_3); (b) for hydrogen peroxide (H_2O_2); (c) for phosphorus trichloride (PCl_3); (d) for the perchlorate ion (ClO_4^-); (e) for ethylene ($\text{H}_2\text{C}=\text{CH}_2$); (f) for sulfur dioxide (SO_2).
7. Give the nuclear composition of each of the atoms represented in Fig. 162, in terms of alpha particles, protons, and neutrons.
8. What are the projectiles which have been used for producing nuclear reactions?
9. What is the mechanism by which an atom is supposed to be able to absorb or to give out radiant energy in terms of the Bohr theory?
10. How many electrons are there (a) in a gram-atom of carbon? (b) in a gram-atom of tungsten? (c) in a gram-molecule of carbon dioxide? (d) in a gram-ion of aluminum?

Problems

1. Argon (at. no. 18, at. wt 39.944) consists of two isotopes of mass numbers 39 and 41. In what ratio are these two isotopes present in argon?
2. Thorium (at. no. 90, at. wt 232), like uranium, is the head member of a radioactive disintegration series. Thorium loses an alpha particle to form mesothorium 1, which in turn loses a beta particle to form mesothorium 2.
(a) What are the atomic weights of MsTh1 and MsTh2? (b) What are the atomic numbers of MsTh1 and MsTh2? (c) If thorium is placed in Group IV of the periodic table, in what groups are MsTh1 and MsTh2 placed?

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- DAVIS. *The Advance of Science*. Chapter V tells the story of the birth of nuclear chemistry in nontechnical language; Chapter VI deals with energy from atoms.
- JAFFE. *Crucibles*. Chapters XIV-XVI and the Epilogue give us a glimpse into the lives of the men whose discoveries led to our present-day conception of the structure of the atom.
- MILLIKAN. *Electrons, Protons, Photons, Neutrons, and Cosmic Rays*. A valuable book for those who may wish to dip deeply into the subject.
- NOYES and NOYES. *Modern Alchemy*.
- ROBERTSON. *Atomic Artillery*. A nonmathematical and popular treatise (177 pages) that tells the story of electrons, protons, positrons, photons, neutrons, and cosmic rays, and explains the game of "shooting atoms" and of "turning one element into another."
- RUTHERFORD. *The Newer Alchemy*. A little book of 67 pages. It tells of "The Transmutation of Elements, how it has been accomplished, and what it means."
- TILDEN and GLASSTONE. *Chemical Discovery and Invention in the Twentieth Century*. Chapter VIII is entitled "Structure and Disintegration of Atoms."

CHAPTER 15

Solutions; Concentration; Molecular Weights

Mixtures, solutions, and compounds. In Chapter 2 a distinction was made between a *mixture* and a compound. The term *mixture*, as ordinarily used by the chemist, designates a system of at least two constituents the individual particles of which can be distinguished from one another by visual observation, aided by the microscope if necessary. The term is customarily broadened to include *solutions*. A solution is also a mixture, of at least two different substances. But it is a homogeneous, or even, mixture, in the sense that its different kinds of particles are so fine-grained that they cannot be distinguished in the most powerful microscope. A solution is really a mixture of different varieties of molecules (or atoms or ions), and these particles are beyond the reach of the microscope.

The principal difference between a solution and a compound (which is also homogeneous) is that a solution may have a variable composition, whereas a compound, as we know very well, always has a perfectly definite composition, and every particle is exactly like every other one. A solution is defined as *a homogeneous mixture whose composition may be varied continuously between certain limits.*

Constituents and varieties of solutions. One constituent of a solution (usually the more abundant one) we think of as the medium in which the other (less abundant) constituent is dissolved; the medium we call the *solvent*, the dissolved constituent the *solute*. Since, before the solution is made, the solvent-to-be and the solute-to-be can each be either a gas, liquid, or solid, we see that there are nine possible combinations (3×3), or nine general kinds of solutions possible. Five of the most important pairs will now be considered.

Solutions of gases in gases. We rarely think of a mixture of two gases as a solution; yet it conforms to our definition. Save when obvious chemical action occurs, gases mix in every proportion and apparently have no effect upon one another. When dealing with a solution of gases, we may assign to each *its fraction of the total pressure*, which will be the same as though the other gases were to be removed, leaving the one alone in the enclosing volume (Dalton's

law, p. 71). Since there is practically no expansion or contraction when gases are mixed, the density of the mixture can be calculated from the known densities and percentages of the constituent gases.

Solutions of gases in liquids. While gases mix with each other in all proportions, a liquid will dissolve but a limited quantity of a gas; and when this limit is reached, the liquid is said to be *saturated*. Under these conditions the ratio of the quantity of the gas solute to the liquid solvent is called the *solubility* of the gas (under definite conditions of temperature and pressure). This may be expressed in a variety of ways, the most prevalent usage being to state the number of volumes of gas dissolved in one hundred volumes of the solvent.

Solubility of Gases in 100 cc of Water

NAME OF GAS	AMOUNT DISSOLVED AT 0° AND UNDER 760 MM PRESSURE	
	Grams	Cubic Centimeters
Ammonia	100.1192	129,890.00
Hydrogen chloride	82.9738	50,600.00
Sulfur dioxide	23.3513	7,979.00
Hydrogen sulfide	0.6726	437.00
Carbon dioxide	0.3386	171.30
Oxygen	0.0070	4.96
Nitrogen	0.0029	2.33
Hydrogen	0.0002	2.14

In respect to solubility, gases fall roughly into two classes: those of rather small solubility, such as oxygen, nitrogen, and hydrogen; and those of much larger solubility, such as ammonia, hydrogen chloride, and sulfur dioxide. These groups will be described separately.

Factors affecting the solubility of sparingly soluble gases. A number of different factors affect the solubility of a little-soluble gas.

1. Effect of specific properties. The individual properties of both gas and liquid are of the first importance in fixing the solubility of a given gas in a given liquid. All gases are soluble to some extent in every liquid. Other conditions being equal, no two gases have the same solubility in a given liquid.

2. Effect of pressure; the law of Henry. This law was formulated by the English chemist Henry (1775-1836), and may be stated as follows: *The weight of a gas that dissolves in any given liquid is directly proportional to the pressure, provided the temperature remains constant* (Fig. 171). If 1 g of a gas dissolves in 100 cc of water at atmospheric pressure, 2 g will dissolve under 2 atm., provided the

temperature remains constant. Under high pressures relatively large quantities of a gas dissolve; and when the pressure is diminished, a proportional weight of the gas escapes, as fine bubbles (*effervescence*).

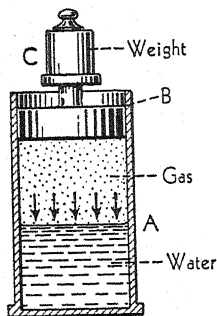


FIG. 171. *Henry's Law*

A gas standing over water in the cylinder A, under a pressure of the weight which is placed on the tight-fitting piston B

When a mixture of two or more gases is maintained over a liquid, *each dissolves independently of the others and in accordance with its own partial pressure*. This is a necessary consequence of the law of Dalton (p. 71), which states that each gas in a mixture exerts its own partial pressure independently of the others. Each gas therefore dissolves independently of the others, in accordance with Henry's law.

3. Effect of temperature. With rise in temperature, gases become *less soluble*, and at the boiling point of the solvent no sparingly soluble gases are left in solution; so all the gas is driven out by boiling the solution.

Factors affecting the solubility of very soluble gases. In a *qualitative* way very soluble gases are affected by temperature and pressure in the same way as sparingly soluble ones; but *quantitatively* the law of Henry does not hold, for the solubility is no longer proportional to the pressure. The specific properties of both gas and liquid play a prominent part, leading to very wide differences in solubility, as may be seen in the table on page 253 and by reference to Fig. 172. There is always a very considerable change in the volume of the solvent when a large volume of gas is absorbed; and it is not possible to calculate the density which such a solution will have,

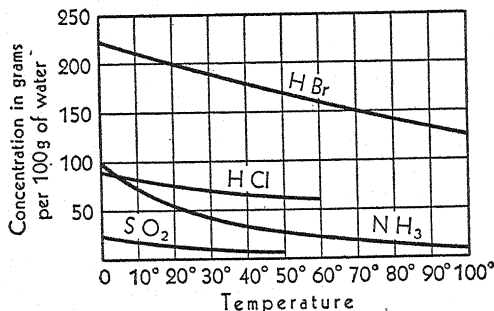


FIG. 172. *Curves Showing the Solubility of Some Very Soluble Gases Bubbled through Water in an Open Vessel (Atmospheric Pressure)*

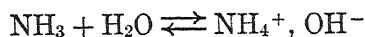
or from its measured density to infer the weight of gas it has absorbed. Thus, 1 l of water, when saturated with ammonia at 14°, increases in volume to 1.580 l, while its density decreases to 0.8844.

Solutions of this kind frequently acquire properties not possessed by either the gas or the liquid. Neither ammonia nor water has any

effect on the color of red litmus (an organic dye), whereas the solution turns it blue; similarly, sulfur dioxide has no effect on blue litmus, while the solution turns it red. For these and many other reasons it is certain that a chemical action takes place between the gas and the solvent, which accounts for high solubility. On the other hand, when the two solutions just mentioned are exposed to the open air, ammonia and sulfur dioxide respectively escape from solution, and carbon dioxide also escapes from its solution in water (Fig. 173), just as do gases which give no evidence of chemical combination.

While it is true that gases are more soluble in cold water than in warm water, they will not dissolve in ice. As water in tanks freezes from the outside inward, the dissolved air is liberated as bubbles, which are pushed ahead of the advancing front of ice crystals toward the interior. For the same reason it is not wise to allow bottles of soda water or of other carbonated waters, placed, say, in the tray of an automatic refrigerator, to become cold enough to freeze the water. The considerable quantity of carbon dioxide gas thus liberated in the small free space of the bottle may develop sufficient pressure to cause a violent explosion. Such cases have been reported.

Chemical equilibrium in solution. The exceptional behavior of solutions of very soluble gases is probably to be explained in terms of a chemical equilibrium existing in the solution. For example, the solution of ammonia in water may be represented by the equilibrium equation



which indicates that the ammonia combines with water to form a compound, ammonium hydroxide ($\text{NH}_4^+, \text{OH}^-$), but that the reaction is incomplete, owing to the decomposition of the compound into its original components. The equation therefore represents an equilibrium similar to that between oxygen and ozone, or between water and its constituents, oxygen and hydrogen.

Solutions of liquids in liquids. Two liquids may conduct themselves toward each other in either of two ways: they may each reach a definite limit of saturation with the other, or they may be freely soluble (or miscible) in all proportions.

Freely miscible liquids. A number of familiar liquids mix freely with (dissolve in) water in all proportions; among these are alcohol,



FIG. 173. Showing Escape of Carbon Dioxide When the Pressure of the Gas on a Solution Is Relieved by Removal of Cap

glycerin, and many acids, like nitric, sulfuric, and acetic. Many oils and fats are also miscible with each other in all proportions. In some cases, as with alcohol and water, each liquid appears to retain its own chemical characteristics in solution; in other cases, especially with acids dissolved in water, new chemical characteristics are acquired along with the old ones, suggesting the existence of some such chemical equilibrium as that described in connection with ammonia. Several properties of liquid solutions are of importance.

1. *Vapor pressure.* Before mixing, each liquid has its own characteristic vapor pressure at the temperature in question. After mixing, it is found that each liquid has diminished the vapor pressure of the other, so that the vapor pressure of the solution is never as great as the sum of the two original pressures. It may be greater or less than that of either liquid taken separately, or it may have an intermediate value. It also depends on the relative concentrations of the two liquids. In any case the vapor from the solution at any definite temperature will be a mixture of that of each liquid, provided each has an appreciable vapor pressure.

2. *Boiling point.* On heating a solution of one liquid in another the total vapor pressure increases; and when it just exceeds the opposing pressure of the atmosphere, the solution boils. From what has been said in regard to the vapor pressure of solutions it will be seen that we can form little idea as to the boiling point of a solution from the known boiling points of its constituents. It may be lower or higher than that of either constituent. Usually it has an intermediate value. Since the ratio by weight of the two vapors escaping from the solution is not in general the same as that of the two liquids constituting the solution, the composition of the liquid will change during the process of boiling. This will lead to variations in the composition of the vapor and a steady change in boiling point. It is only under exceptional conditions that a solution has a constant boiling point (and a constant composition) during distillation.

3. *Fractional distillation.* In distilling a solution the component having the greater vapor pressure will in general pass away from the solution more rapidly than the one of lower vapor pressure (higher boiling point). If the vapors are condensed, as described in the distillation of water, and the resulting liquid is collected in successive portions by changing the receiver at intervals, the first portions will be richer in the more volatile constituent, and the higher-boiling liquid will be largely obtained in the later portions. By repeating the process with each portion obtained in the first operation the two liquids may in time be separated from each other.

Such a process is called *fractional distillation*. It is of the greatest importance in many industries, such as the refining of petroleum and the manufacture of alcohol and glycerin. We have already seen that nearly pure oxygen is prepared from liquid air by this process.

4. Constant-boiling solutions. It occasionally happens that there is one particular concentration of a solution which has a lower vapor pressure (higher boiling point) than any other concentration or than that of either constituent taken separately. When such a solution is distilled, one or the other constituent vaporizes more readily, and the concentration tends toward that of lowest vapor pressure. When this concentration is reached, the solution boils with constant boiling point like a pure substance, and the distillate has the same composition as the solution remaining in the still. Such a constant-boiling solution cannot be altered in composition by repeated distillation (under a given pressure). An example of such conduct is found in aqueous solutions of nitric acid, the constant-boiling solution consisting of 68 per cent acid and 32 per cent water. The constant-boiling solution of sulfuric acid contains 98.33 per cent acid, while that of hydrochloric acid contains 20.24 per cent of the acid, provided the pressure is standard (760 mm).

Constant-boiling solutions of maximum vapor pressure and minimum boiling point are also known.

Sparingly miscible liquids. If water is shaken for a few moments with ether or chloroform in a bottle and set aside for a short time, the more or less turbid liquid gradually clears and two liquid layers form, with the one of smaller density floating on the heavier. Each of these layers is a saturated solution. In the case of ether and water the upper layer consists of ether saturated with water; the lower, of water saturated with ether. With some pairs of liquids, especially if certain foreign materials are present, this parting into two layers is very slow. The liquid may remain turbid for some time and is called an *emulsion*. The name suggests a conspicuous example, namely, milk.

Solutions of solids in liquids. A solid dissolved in a liquid is by far the most familiar type of solution. In the following paragraphs it should be remembered that we are dealing with true solutions only. Thus, it is sometimes said that zinc dissolves in hydrochloric acid. In this case, however, the solution is preceded by a chemical reaction whereby the zinc is converted into zinc chloride, and it is this compound which is obtained when the solution is evaporated. With solutions such as we are now considering, evaporation leaves the solute in its original chemical condition.

Concentration. The term *concentration* is much used by chemists, and its meaning is a very significant one. It refers in a general way

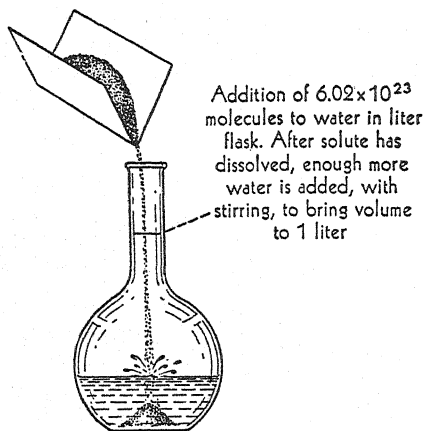


FIG. 174. Preparation of Molar Solution

to the strength of a solution, and the word is almost synonymous with *crowdedness*, that is, the crowdedness of solute particles in a solution. We speak of dilute solutions, or solutions of small concentration, as contrasted with concentrated solutions. But these are merely relative terms. To state the concentration definitely we must state the *quantity of solute and the quantity of solvent or solution*. Sometimes the concentration is stated on a percentage basis, but it is often more desirable to state the num-

ber of *gram-molecular weights* which a given volume of the solution contains. When one gram-molecular weight of a compound is dissolved so as to make a liter of solution, the product is said to be a molar (or gram-molecular) solution. Thus, a molar solution of sodium hydroxide (NaOH) contains 40.005 g of the compound in 1 l, while that of nitric acid (HNO_3) contains 63.016 g. If 15 g of sodium hydroxide is dissolved so as to form 1 l of solution, the concentration is 0.375 molar ($15 \div 40.005$).

Concentration is independent of quantity of solution. If the molar solution made up, as in Fig. 174, is a solution of sugar, then 1 l of solution contains 6.02×10^{23} sugar molecules; and 1 cc contains 6.02×10^{20} sugar molecules. Yet the two quantities of the solution have the same concentration. For, while 1 cc contains only $\frac{1}{1000}$ as many solute molecules, its volume is only $\frac{1}{1000}$ as great as the liter. The degree of "crowdedness" is the same in both. By dipping up or pouring out the proper number of cubic centimeters of a molar solution, one can measure out a required number of molecules, or measure out a known fraction of a gram-molecular weight.

Saturated solutions. When a lump of sugar is placed in a small beaker and covered with water, as represented in Fig. 175, it gradually diminishes in size and passes into solution; that is, particles leave it to wander through the solvent. If there is enough sugar, and if a long enough time elapses, the concentration of the sugar in the solution reaches a *definite limiting value*; and we say that the sugar

ceases to dissolve and that the solution is *saturated*. There is good reason for thinking that molecules continue to leave the lump after saturation has been reached, but that others return to it from the solution. In time an equilibrium will be reached: the rate of departure of the molecules will be equal to the rate of their return. A *saturated solution* may therefore be defined as *one which is in equilibrium with the undissolved solute*.

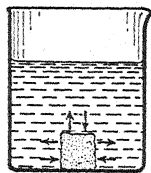


FIG. 175 Diagram illustrating the Equilibrium of a Saturated Solution

A saturated solution may be obtained in a quicker way. Most solids are more soluble in hot liquids than in cold. If we approximately saturate a solution at a higher temperature and then reduce the temperature to the desired point, *taking care to have some of the solid present all the time*, the excess of the solute will crystallize out, and almost at once the solution will come to the same concentration as was reached in the slower way.

Rate of solution. Unless a solution is constantly stirred, it takes a long time to bring about saturation. The portion of the liquid in immediate contact with the solid dissolves it rapidly at first, then more and more slowly as saturation is approached. Meanwhile the dissolved molecules make their way, or *diffuse*, very slowly into the portions of the solvent not in contact with the solid. Thus, if some crystals of a highly colored substance, such as potassium permanganate, are placed in the bottom of a tall vessel full of water, it will take weeks or even months for the solution to become uniformly colored. Vigorous stirring rapidly brings all the solvent into contact with the solid, and approximate saturation is reached in a few minutes; but even then *complete* equilibrium is reached slowly at constant temperature.

Supersaturated solutions. If we neglect to have some of the solid present while a concentrated solution cools, it may happen that the excess of solute will fail to crystallize out. The solution will then contain *more than the normal saturation quantity of the solute*, and is said to be *supersaturated*. This is apt to occur in the case of very soluble solids, with salts containing much water of hydration — for example, with sodium sulfate ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$), sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$), and ferric nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) — and, in general, in all cases where the solution becomes notably viscous. It must be remembered that saturation is normally an *equilibrium*; and when one member of the equilibrium is absent, abnormal results may be expected. The introduction of even the smallest fragment

of the solid solute into a supersaturated solution will bring about the crystallization of the excess of solute.

Effect of temperature on solubility. Change of temperature always changes the solubility of a solute. As a rule, solids are more

soluble in hot than in cold solvents, though occasionally the reverse is true. Many compounds of calcium, including the hydroxide, $\text{Ca}(\text{OH})_2$, are of the latter class, while the solubility of common salt is very little affected by the temperature. Fig. 176 shows the change in solubility in a few familiar cases.

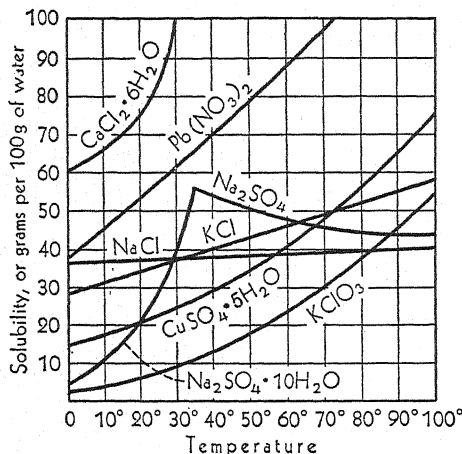


FIG. 176. Solubility Curves of a Few Compounds

tion of the solids separating above and below this point shows that they are not the same. Below 32.4° the solid is $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, while above this point it is the anhydrous salt Na_2SO_4 . The point 32.4° , therefore, marks the temperature at which one salt changes into the other; like the freezing point of a liquid, it is called a *transition point*. Sharp breaks like this in a solubility curve always suggest some chemical transformation in the solute, so that the study of such curves is of great importance in giving information as to the changes taking place during a process of solution.

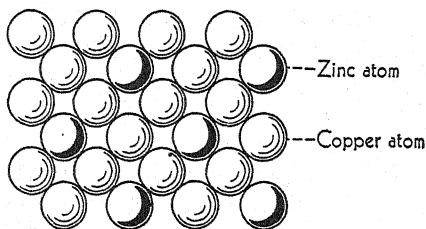


FIG. 177. Ordinary Brass Is a Solid Solution of Copper and Zinc Mixed in the Ratio of About 3 of Copper to 1 of Zinc

Solutions of solids in solids. A number of cases have been noted in which one solid slowly diffuses into another. Gold will diffuse into lead, and lead into gold, when clean pieces of the two metals are tightly clamped together; copper-plated zinc gradually turns lighter in color from mutual diffusion of the two metals. The products in such cases are called *solid solutions*. Similar solutions can be prepared

in special cases by melting the two solids together. If they form a liquid solution, they may also freeze as a homogeneous solid with the properties of a true solution (Fig. 177). (In other cases solid solutions are not formed; one solid or the other separates as a pure material, or definite compounds form).

Heat of solution. When any crystalline solid dissolves, there is always a change in the temperature of the solvent. As a rule the temperature falls, indicating absorption of heat; and this is always true if the solid is more soluble in the hot solvent than in the cold. In case the solid is more soluble in the cold solvent, heat is evolved by the act of solution. The heat evolved or absorbed by 1 g of the solid to form a dilute solution is called the *heat of solution*. This value multiplied by the molecular weight is the *molecular heat of solution*. Heat is also absorbed when a very concentrated solution is diluted, and this is called the *heat of dilution*.

Frequently the solid combines with the water to form a stable compound as it passes into solution. Such an action may evolve much heat and so conceal the cooling effect of solution. For example, the anhydrous calcium chloride used in drying gases combines with water to form the stable compound $\text{CaCl}_2 \cdot 6 \text{H}_2\text{O}$, with great evolution of heat.

EFFECT OF SOLID SOLUTE ON PROPERTIES OF SOLVENT; METHODS FOR DETERMINING MOLECULAR WEIGHTS

Properties of a solvent modified by a solute. The properties which a solvent (such as water) possesses when pure are often greatly modified when a solid is dissolved in it. Among these properties are (1) *vapor pressure*, (2) *boiling point*, (3) *freezing point*. These effects are not only interesting and important in themselves, but on them are based methods for finding the molecular weights of solutes. In the present treatment we shall deal only with covalent solutes, which *do not furnish ions*; in the next chapter solutions of electrovalent compounds will be considered.

1. **Lowering of the vapor pressure.** The fact that a solution of sugar in water has a smaller vapor pressure (aqueous tension) than water itself can be easily shown with a manometer (Fig. 178). No completely satisfying explanation for the lowering is known. Perhaps the sugar molecules act as a "screen" and interfere with the escape of solvent molecules, and so lower the vapor pressure.

After many years of careful experimental work, the French scientist Raoult found (1) *that the lowering of vapor pressure is directly*

proportional to the concentration of the solution, and (2) that the effect is the same for all solutes, regardless of their chemical nature, provided

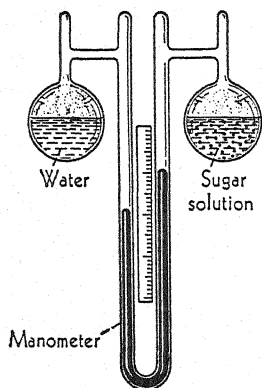


FIG. 178. *The Air Is Pumped Out of the Apparatus. Then the Difference in Levels of the Mercury Columns Gives the Difference in Pressure between the Water and the Solution*

they are neither electrovalent compounds nor liquids with appreciable vapor pressure. In other words, at a given temperature the lowering of the vapor pressure of a given solvent depends only on the number of solute molecules in a given quantity of the solvent.

Deliquescence. When exposed to moist air, many solids absorb water to such an extent that they gradually pass into solution. This spontaneous process is called *deliquescence*, and the solid is said to be *deliquescent*. The explanation of this process is as follows:

Apparently all solids tend to condense a film of moisture on their surface, and the film soon becomes a saturated solution by dissolving the solid. If the solid is very soluble, the solution so formed will be very concentrated, and its vapor pressure very small. If the vapor pressure of the solution should be smaller than the average value for the partial pressure of the water vapor normally present in air (which may be taken as about 12 mm at ordinary temperatures), then this solution cannot possibly evaporate. On the contrary, it will absorb moisture from the air. This will dilute the solution, which will then dissolve more of the solid, and the process will continue until all the salt has dissolved. To say that a salt is deliquescent, in a climate of average moisture, is really to imply that it is very soluble.

2. Elevation of the boiling point. Since the boiling point of a liquid is the temperature at which its vapor pressure just exceeds the opposing pressure of the atmosphere, it is evident that any condition which lowers the vapor pressure will raise the boiling point, since the liquid will have to be heated to a higher temperature to regain its original vapor pressure. Raoult found it to be true that the lowering of vapor pressure is almost exactly proportional to rise of boiling point. It follows that gram-molecular weights of any substances not electrovalent and not having a vapor pressure of their own, when dissolved in a definite weight of a solvent, produce the same rise in the boiling point. But the rise is different for different solvents. The boiling point elevation produced by 1 g-mol. wt of solute added

to 1000 g of water is 0.518° , and is called the *boiling-point constant* for water.

Molecular weight by the boiling-point method. The boiling point of water is first read off on a very sensitive thermometer (which has a large bulb of mercury, a fine capillary stem, and a scale covering only a few degrees just above 100°). Then a known weight of solute is dissolved in a known weight of water, and the boiling point rise of the solution is noted (Fig. 179). This is all the information one needs to calculate the molecular weight of the solute. The method is really a scheme for counting off a definite number of solute molecules. Let us illustrate with an actual case.

Example. Measurement showed that 0.750 g of the compound urea (a solid), dissolved in 25.0 g of water, raised the boiling point 0.259° . What is the molecular weight of urea?

Since the concentration of a solution is independent of the quantity of solution, let us suppose that we are dealing with 1000 g of water, instead of 25.0 g. This is 40 times as much, and would contain 40 times as much solute, namely $40 \times 0.750 \text{ g} = 30.0 \text{ g}$ urea. This quantity of solute raises the boiling point 0.259° , which is just *half* of 0.518° , the boiling-point constant. Therefore just *half* of a gram-molecular weight of the solute is present; then $2 \times 30 \text{ g} = 60 \text{ g}$ must be the gram-molecular weight of urea. The result corroborates the formula which has been proposed for urea, $\text{CO}(\text{NH}_2)_2$, which indicates a molecular weight of about 60.

3. Lowering of the freezing point of the solvent. When an unsaturated solution is cooled sufficiently, it does not freeze as a *solution*, but crystals of the *pure solvent* are formed, and at a temperature below the true freezing point of the solvent. Doubtless one of the first observations of this kind was that salt water remains unfrozen while fresh water close by freezes. It is to lower the freezing point of water that we add various compounds (sometimes sugar, but usually alcohol, glycerin, or ethylene glycol), to the water in an automobile radiator in cold weather.

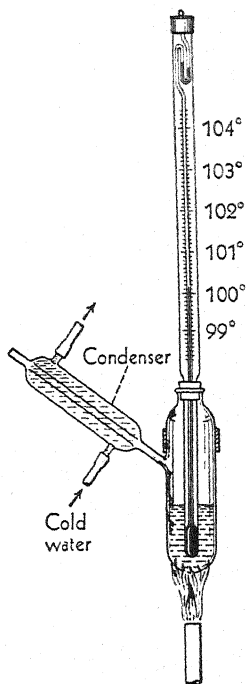


FIG. 179. Showing the Principle of the Boiling-Point Method

The condenser prevents the escape of the vapor of the solvent. The thermometer bulb must be immersed in the solution. If it were in the condensing vapor, above the solution, it would register the boiling point merely of the solvent

Lowering of the Freezing Point of Water

SOLUTE	FORMULA	LOWERING PRODUCED IN 1000 G OF WATER BY 1 G-MOL. WT. OF SOLUTE
Methyl alcohol (methanol)	CH_4O	1.86°
Ethyl alcohol	$\text{C}_2\text{H}_6\text{O}$	1.83°
Sucrose (common sugar)	$\text{C}_{12}\text{H}_{22}\text{O}_{11}$	1.86°
Glycerin	$\text{C}_3\text{H}_5(\text{OH})_3$	1.92°
Urea	$\text{CO}(\text{NH}_2)_2$	1.86°

Molecular weights by the freezing-point method. The same reasoning that enables us to determine molecular weights by the rise of the boiling point can be applied to the lowering of the freezing point. A gram-molecular weight of a covalent solute, dissolved in 1000 g water, lowers the freezing point of the water by approximately 1.86° (called the *freezing-point constant* for water).

Every *solvent* has its own characteristic freezing-point constant; thus for acetic acid it is 3.9° , for benzene 5.4° , for naphthalene 6.8° .

Freezing-point apparatus. The Beckmann apparatus is represented in Fig. 180. The weighed liquid (water) is placed in the inner tube *A*, and the thermometer arranged to dip into the liquid. A suitable stirrer is also provided. The tube *A* is hung in a larger tube *B*, which is empty, and the latter is surrounded by a cooling mixture of ice and salt. This cools the air in *B* below the freezing point of water, and makes it possible to freeze a portion of the liquid in *A*. The thermometer is of special construction, so that changes of temperature as small as 0.001° can be read. The freezing point of the pure water, and also the freezing point after the introduction of a weighed quantity of the compound whose molecular weight we wish to determine, give the data for the calculation.

Example. In an experiment 0.46 g of sugar, dissolved in 20.3 g of water, produced a lowering of 0.126° . The proportion

$$20.3 : 1000 = 0.46 : x; \text{ whence } x = 22.7$$

gives the weight which would produce the same lowering if the sugar were dissolved in 1 l of water. But a gram-molecular weight would produce a lowering of 1.87° , so that 22.7 g constitutes $0.126 \div 1.86$ of a gram-molecular weight of sugar. The molecular weight as determined by this experiment

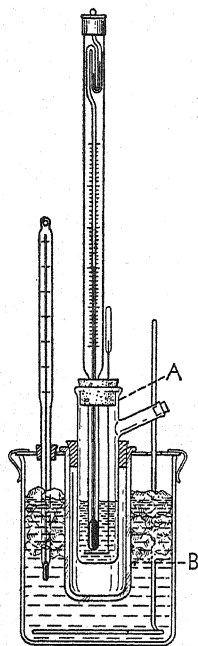


FIG. 180. The Beckmann Apparatus for Determining Molecular Weights

is therefore about 337. This is only approximate (the correct weight is 342), since the method, like all our methods for determining molecular weights, usually gives only approximate results.

Lowest freezing point of solutions. If we cool a *dilute* solution, crystals of the solvent are formed; and if we continue the cooling, the solution grows more and more concentrated, owing to the removal of the solvent as crystals. Finally it becomes *saturated*, and then crystals of *both solvent and solute* are formed. The temperature at which this happens is the lowest freezing point of the solution. The resulting solid, consisting of two kinds of crystals in fixed proportion, is called a *eutectic*; and the temperature at which the eutectic freezes is called the *eutectic temperature*.

Freezing mixtures. It is a familiar fact that when we put ice into water at room temperature, the temperature of the mixture falls to the freezing point of water because of the absorption of heat by the melting of the ice. In like manner, if we mix ice, water, and a soluble solid, the temperature will fall to the eutectic temperature, provided there is enough ice and solid solute present (and if the mixture is well insulated). The absorption of heat is due to both the melting of ice and the dissolving of the solid solute. The more soluble the solute, the lower the eutectic temperature. We often make use of a mixture of crushed ice and solid salt as a freezing mixture to secure temperatures somewhat below 0°. The eutectic temperatures (sometimes called cryohydric temperatures when *water* is the solvent) of a few salt mixtures are shown in the following table:

Eutectic (or Cryohydric) Temperatures of Ice and Various Salts

SALT	TEMPERATURE	SALT	TEMPERATURE
Potassium nitrate . . .	- 3°	Sodium nitrate . . .	- 18.5°
Sodium thiosulfate . . .	- 11°	Sodium chloride . . .	- 22.4°
Ammonium chloride . . .	- 15.8°	Calcium chloride . . .	- 54.9°
Ammonium nitrate . . .	- 17.5°	Hydrogen chloride . .	- 86.0°

Osmosis. Closely related to the lowering of the vapor pressure, to the elevation of the boiling point, and to the depression of the freezing point is the phenomenon of *osmosis*. It is the passage of a solvent from a dilute solution (or from a pure solvent) through a membrane into a more concentrated solution.

Probably almost everyone has had the experience of setting aside a saucer of fresh strawberries covered with sugar, only to find some-time later that the berries are shriveled and the saucer filled with sweet juice. What happens is this: A concentrated sirup is formed

around the skin of the berries by some of the sugar which dissolves in the superficial water. Then water, in considerable quantity, from the inside of the berries passes through the skin into the concentrated sugar solution. The skin is a so-called *semipermeable* membrane; that is, it will allow molecules of solvent to pass readily but will not allow molecules of solute to pass.

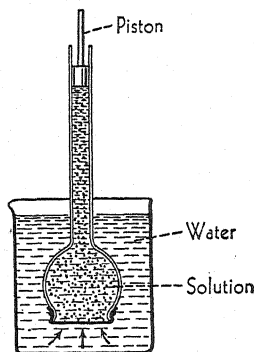


FIG. 181. Diagram Illustrating Meaning of Osmotic Pressure

Osmotic pressure. A semipermeable membrane, such as a piece of parchment paper or nonwaterproof cellophane, is fastened tightly over the bell of a thistle tube with cord and sealing wax (Fig. 181). A sugar solution is placed in the vessel so constructed, which is then immersed in pure water. Osmosis starts, and the volume of the sugar solution slowly increases as the water enters through the membrane. Now, if we could fit the tube with a piston, as shown in the illustration, and with it apply a sufficiently large pressure on the solution, osmosis would stop. In fact, by pushing hard enough on the piston, water could be squeezed out of the solution, through the membrane, back into the outer vessel.

That pressure which, when applied to a solution, will just prevent the entrance of solvent into it through a semipermeable membrane is the osmotic pressure of the solution. The pressure need not be applied by piston. The hydrostatic pressure of a long vertical column of the solution may serve the same purpose.

Quantitative measurements. An apparatus such as the one just described is not adapted to the exact measurement of large osmotic pressures, because the membrane is not strong enough to withstand the pressure. A very satisfactory method for strengthening and supporting such a semipermeable membrane has been developed by Morse. The membrane is formed by precipitating the compound known as copper ferrocyanide as a film within the body of the walls of a fine-grained, unglazed porcelain cell (A, Fig. 182). Such a mechanically supported membrane will withstand a pressure of as much as 100 atm.

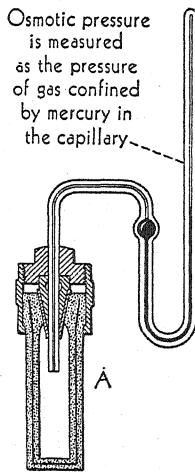


FIG. 182. An Apparatus for Measuring Osmotic Pressure

The laws of osmotic pressure. The results of extensive experimental study of osmotic pressure show that for covalent compounds it (1) is approximately proportional to concentration, (2) is independent of the nature of the solute particles, and (3) is proportional to the absolute temperature. Such behavior recalls the gas laws. Indeed, it has been found to be true that the *osmotic pressure of a solution is approximately equal to the gas pressure which the solute would exert if it were a gas occupying the same volume as the solvent, at the same temperature.*

For instance, 1 g-mol. wt of a gas, in 22.4 l at 0°, exerts a pressure of 1 atm. At 20° the pressure is $\frac{293}{273} \times 1 \text{ atm} = 1.07 \text{ atm}$. Similarly, 1 g-mol. wt of sugar dissolved in 22.4 l of water, at 20°, has an osmotic pressure of about 1.07 atm.

Questions

1. Distinguish between the following terms and give an example to illustrate each: (a) *element*; (b) *compound*; (c) *mixture*; (d) *solution*; (e) *solvent*; (f) *solute*; (g) *saturated solution*; (h) *supersaturated solution*; (i) *molar solution*.

2. State each of the following laws and give an example to illustrate each: (a) law of Henry; (b) law of Dalton. (c) Do these laws hold for all gases?

3. Suppose you wished to dissolve as much as possible of (a) a gas in a liquid; (b) a solid in a liquid. In a general way how would you proceed?

4. Do you know (a) of any gas that is more soluble in hot water than in cold? (b) of any solid that is more soluble in cold water than in hot?

5. What is the solubility of each of the following compounds in water at the temperature designated: (a) lead nitrate at 50°; (b) sodium chloride at 70°; (c) copper sulfate at 40°?

6. If we know the density of a solvent and of a solute, is it possible to calculate the density of the resulting solution?

7. How could you separate (a) a gas dissolved in a liquid; (b) a liquid dissolved in a liquid; (c) a solid dissolved in a liquid?

8. In what ways are the properties of a solution of a solid in a liquid similar to the properties of a solution of a gas?

9. Suppose you were given the problem of finding some liquid that could be safely and economically used in the radiator of an automobile in cold weather. (a) What properties must such a liquid have? (b) How would you proceed to find or produce these properties in a liquid?

10. Ordinary alcohol has a density of 0.789. Suppose you have equal volumes of two solutions: the one contains 3.5 per cent of alcohol by volume, and the other 3.5 per cent by weight. Which solution would contain the larger weight of alcohol?

Problems

1. Calculate the number of grams of each of the following compounds required to make 1 l of a molar solution: (a) sodium chloride (NaCl); (b) calcium chloride (CaCl_2); (c) potassium nitrate (KNO_3).

2. Would it be possible to prepare a molar solution of calcium sulfate (CaSO_4)?

3. One hundred cubic centimeters of water dissolves 4.96 cc of oxygen under standard conditions; an equal volume of water dissolves 2.33 cc of nitrogen under the same conditions. Suppose that air were enclosed over 100 cc of water under standard conditions. (a) Calculate the number of cubic centimeters of oxygen and of nitrogen that would be dissolved. (b) How would the ratio of free oxygen to nitrogen in the dissolved gases compare with their ratio in the air?

4. A solution of 5.52 g of glycerin in 40 g of water was found to raise the boiling point 0.777° . What is the molecular weight of glycerin?

5. Ordinary alcohol, $\text{C}_2\text{H}_6\text{O}$, is a covalent compound. Suppose the radiator of an automobile held 12 l and you wished to fill it with an aqueous solution of alcohol that would remain liquid at -10° . Calculate the approximate weight of alcohol required.

6. What osmotic pressure would be developed by a solution of 4.4 g of dioxane (formula, $\text{C}_4\text{H}_8\text{O}_2$) dissolved in 280 cc of water at 15° ?

Reading References

CHAPIN and STEINER. *Second Year College Chemistry*. Chapter XIV is entitled "Freezing Points and Boiling Points of Solutions; Osmotic Pressure."

CLARKE. *Marvels of Modern Chemistry*. Chapter VII is entitled "Solutions and Physical Chemistry."

TILDEN and GLASSSTONE. *Chemical Discovery and Invention in the Twentieth Century*. Chapter IX deals with solutions.

Ionization in Solutions

Introduction. In previous pages ions have been defined as electrically charged particles — atoms, or groups of atoms. We have seen that ions are formed in gases under certain conditions (p. 47) and that solid crystals of electrovalent compounds consist of oppositely charged ions in orderly arrangement (p. 41). We have occasionally assumed that there are ions in solutions; and since so many reactions are carried out in solution, it is important to inquire into the evidence for *ionization in solution*.

The development of the idea that many compounds in solution are in some way separated into ions took place independently of the demonstration of the existence of ions in gases; indeed, it took place a few years earlier, and long before the demonstration that crystals of electrovalent compounds are composed of ions. We shall first trace the experimental basis for the theory of ionization in solution, and then reconcile as far as possible solution ionization with ionization in gases and in crystals.

Faraday's idea of electrical conduction in solutions. Early in his series of wonderful discoveries about electric currents, Michael Faraday (Fig. 184) became interested in the question How does an electric current pass through a solution? He knew that pure water has almost no conducting ability, but that if the water has dissolved in it certain substances, it becomes a good conductor. In his electrical studies Faraday had to invent names for many things, and he called those substances that give conductivity to water *electrolytes*. Most acids, bases, and salts are electrolytes. Substances that do not give conductivity to water he called *nonelectrolytes* (sugar, alcohol, glycerin). The distinction between electrolytes and nonelectrolytes is practically identical with that between electrovalent and covalent compounds. Indeed, the simplest way of finding out whether a given compound is electrovalent is to test the electrical conductivity of its solution.

Some facts about electrolysis. When a current passes through a solution of an electrolyte, some chemical change always takes place. This change is called *electrolysis*. To study the electrolysis of a solution, two plates of suitable inactive material (*electrodes*) are placed in the solution at some distance apart and connected with

wires from a battery or dynamo (Fig. 183). During electrolysis, decomposition products of the electrolyte are deposited on the electrodes or are concentrated around them. For example, during the electrolysis of a solution of zinc chloride (ZnCl_2), zinc is deposited on the *cathode* (negatively charged), and chlorine is set free at the *anode* (positively charged). Thus the products are delivered at some distance from each other.

Faraday's ions. Faraday was convinced that electricity was in some way carried through the solution loaded in small but very definite quantities on fragments of the electrolyte, and that the carriers of the (+) electricity move toward the cathode and the carriers of the (−) electricity toward the anode. He called these carriers *ions* ("goers"), but never very clearly pictured what they are or how they are formed. It came to be believed that the current disrupted the molecule of the electrolyte, loaded the ions with electricity, and sent them on their way.

The Arrhenius theory of ionization. Some fifty years ago the young Swedish chemist Arrhenius (Fig. 185) was greatly impressed by the recently discovered laws relating to the effects on the physical constants of a solvent produced by gram-molecular quantities of solute (lowering of freezing point and vapor pressure, elevation of boiling point, magnitude of osmotic pressure). He was particularly struck by the fact that electrolytes in solution do not show the regularities of nonelectrolytes (Chap. 15), *but produce excessive effects*. To illustrate this point the following table contrasts the lowering of the freezing point of water by some typical nonelectrolytes with that produced by some electrolytes:

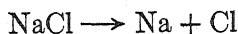
Lowering of the Freezing Point of Water

SOLUTE	CHARACTER	FORMULA	LOWERING PRODUCED IN 1000 g OF WATER BY 1 G-MOL. WT OF COMPOUND
Sugar	Nonelectrolyte	$\text{C}_{12}\text{H}_{22}\text{O}_{11}$	1.86°
Alcohol	Nonelectrolyte	$\text{C}_2\text{H}_6\text{O}$	1.83°
Urea	Nonelectrolyte	$\text{CO}(\text{NH}_2)_2$	1.86°
Hydrogen chloride .	Electrolyte	HCl	3.61°
Hydrogen nitrate .	Electrolyte	HNO_3	3.59°
Potassium hydroxide	Electrolyte	KOH	3.44°
Sodium hydroxide .	Electrolyte	NaOH	3.43°
Sodium chloride . .	Electrolyte	NaCl	3.36°

It will be seen that the electrolytes cause a freezing-point lowering almost twice that caused by the nonelectrolytes. Exactly the same sort of abnormally large effect occurs for boiling-point elevation, vapor-pressure lowering, and osmotic pressure.

Arrhenius imagined that the most natural way to account for the excessively large effects was to assume that there was a *dissociation* (or *parting*) of the electrolyte molecules to give a larger number of particles, and that each such particle had the same effect as a molecule on the lowering of the freezing point of water.

Arrhenius could not maintain that molecules of sodium chloride in solution dissociate into *atoms* of sodium and chlorine,



for all chemists knew that sodium reacts with water to liberate hydrogen, and no hydrogen is evolved when salt dissolves in water. So he assumed that molecules of sodium chloride dissociate into the *ions* Na^+ and Cl^- ,



and that these charged particles have properties different from those of the corresponding atoms. This is in harmony with Faraday's idea of charged carriers in electrolysis, but more definite.

Degree of ionization. The freezing-point lowering produced by 1 g-mol. wt of sodium chloride in 1000 g of water is 3.36° . Now if this were 3.72° , — that is, $2 \times 1.86^\circ$, just twice the lowering produced by a nonelectrolyte, — Arrhenius would have supposed that *all* the sodium chloride molecules were broken up into ions, thus giving *twice* as many particles as were originally present in the solution. The fact that the observed effect, 3.36 , falls short of being *twice* 1.86 would mean that not *all* the sodium chloride molecules are dissociated into ions. It seemed that some of the sodium chloride molecules remained intact, as whole molecules, *undissociated* into ions. The fraction of the total number of molecules (originally

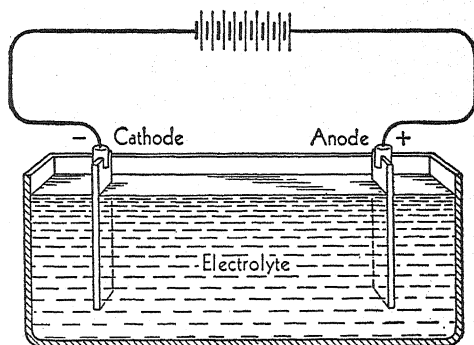


FIG. 183. *The Electrolysis of a Solution of an Electrolyte*

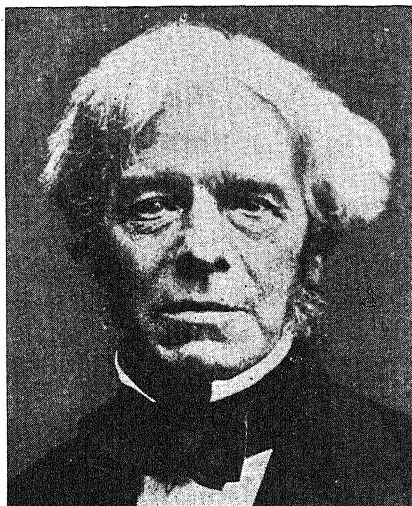


FIG. 184. *Michael Faraday*
(1791-1867)

Pupil of Sir Humphry Davy, and his successor as director of the laboratories of the Royal Institution. One of the world's greatest experimental philosophers both in chemistry and in physics. A pioneer in the liquefaction of gases. The discoverer of benzene, and of the fundamental principles of electrical induction, upon which all electric motors and dynamos depend. He first demonstrated a connection between magnetism and light



Science Service

FIG. 185. *Svante August Arrhenius*
(1859-1927)

Distinguished Swedish chemist, director of the Nobel Institute of the Academy of Sciences, Stockholm. He made many important discoveries concerning the relation between electrolytic phenomena and the physical and chemical properties of compounds. Known chiefly as the founder of the theory of electrolytic dissociation, or ionization. Recipient of the Nobel prize for chemistry in 1903

dissolved) which ionize was called by Arrhenius the *degree of ionization*. In the case of sodium chloride, just considered, the degree of ionization is about 0.80, or 80 per cent. This means that out of every 100 molecules of sodium chloride originally dissolved, 80 ionize and 20 do not. The 80 that ionize split, each of them into two ions ($\text{Na}^+ + \text{Cl}^-$), and thus form 160 ions. These 160 ions added to the 20 undissociated sodium chloride molecules give a total of 180 particles, as compared with the original 100 present before ionization. The number of particles present has thus been increased in the ratio of 180 to 100, or 1.8.

Arrhenius pictured the incompleteness of the ionization of the electrolytes as an equilibrium which was set up between molecules that are decomposing into ions and ions that are combining to form molecules:



It should be noticed that this conclusion does not agree with the later observed fact that in *crystals* of sodium chloride there are no molecules but only ions. Later in the chapter an attempt will be made to find a reason for this difference.

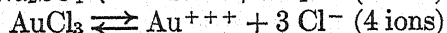
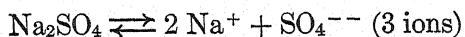
Factors that affect the degree of ionization. The degree of ionization is determined to a small extent by the *temperature*, and in addition to this depends largely on three things:

1. *The nature of the electrolyte (solute).* Electrolytes show great differences among themselves as to the extent to which they give abnormal freezing-point lowerings and other effects to which we have referred. In the table on page 270 some distinct differences in freezing point may be noted among the electrolytes listed. In fact, the degree of ionization may vary all the way from practically nothing up to nearly 100 per cent, depending on the *nature of the electrolyte* itself.

2. *The nature of the solvent.* In some solvents there is a large percentage ionization of an electrolyte. This is especially true of water and to a somewhat less extent of some other liquids, such as liquid ammonia and liquid sulfur dioxide. In some solvents, such as ether and benzene, there is little or no ionization of such electrolytes as are soluble in them.

3. *The dilution.* The effect of dilution on the degree of ionization may be illustrated with sodium chloride. The ratio of the freezing-point lowering of sodium chloride to that of sugar is, as shown above, 1.8 when 1 g-mol. wt of each substance is dissolved in 1000 g of water. Now if both solutions are diluted so that a gram-molecular weight is present in 10 kg, 100 kg, 1000 kg, etc., the freezing-point lowering of both will, of course, become smaller and smaller in the more dilute solutions. *But the ratio of the effects becomes greater than 1.8 and approaches nearer and nearer to 2.0 as the dilution increases.* To Arrhenius, this meant that in very dilute solutions the electrolyte becomes completely ionized. From a kinetic standpoint this is entirely reasonable; for the more widely the ions are scattered through a solution, the less frequently will they have opportunity to recombine, and the equilibrium will move steadily toward a larger proportion of ions as the dilution increases.

Other types of electrolytes. The electrolytes in the table on page 270 dissociate into 2 ions per molecule, but some molecules split up into more than 2 ions. For example,



In the first case, Na_2SO_4 , where the molecule furnished 3 ions, the ratio of the freezing-point lowering, for electrolyte and nonelectrolyte, approaches 3.0 as the dilution increases. In the second case, AuCl_3 , as one would expect, the ratio approaches 4.0.

Conduction of the electric current. Arrhenius found that those solutes which produced abnormally large freezing-point lowerings, boiling-point elevations, and so on, and which he supposed *to be dissociated into ions*, were the very same solutes *which would conduct the electric current*; whereas those dissolved substances, like sugar, alcohol, and others, which behaved normally with respect to freezing-point lowering, and which therefore seemed *not* to dissociate into ions, would *not* conduct the electric current.

These facts lead directly to the conclusion that an electric current can pass through a solution *only if there are charged ions already in the solution*, derived from the dissociation of an electrolyte. The potential at the electrodes does not disrupt molecules of electrolytes into ions (as was formerly supposed), but the ions that carry the current are already present in the solution of an electrolyte.

Assumptions of Arrhenius — Summary. 1. *Formation of ions.* In the process of solution an electrolyte molecule dissociates into two or more ions which move about in the solution as independent particles.

2. *Electric charge of the ions.* An ion differs from an atom or a molecule in that it carries an electric charge acquired in the process of dissociation of the electrolyte molecule.

3. *Positive and negative charges equal.* The ions are of two kinds: the one (cation) is electrically positive, and the other (anion) negative. The sum of the positive charges equals the sum of the negative charges; so the solution remains electrically neutral.

4. *Nonelectrolytes.* Only those compounds that are electrolytes (electrovalent compounds) ionize when dissolved in water. Nonelectrolytes, such as sugar, alcohol, or glycerin, do not ionize, and their solutions are not electrical conductors.

5. *Ionization and equilibrium.* It is assumed that as a rule the ionization of an electrolyte is incomplete and results in an equilibrium between the ions and the undissociated molecules. Since electrical conduction is due to the presence of charged ions, the conductance of a solution should be proportional to the extent or degree of ionization.

Illustrative experiment. The fact that solutions differ greatly in electrical conductance, even at equivalent concentrations, may be demon-

strated with the apparatus represented in Fig. 186. Solutions of equivalent concentrations are placed successively in the bottle *A*, and the wire electrodes are dipped into the solution. Connection with the lighting circuit is made by the cord and plug *B*. If the solution is a good conductor, the current will flow through the lamp *C*, which will then glow.

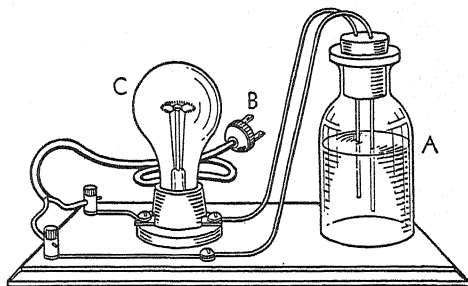
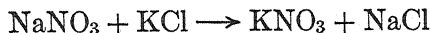


FIG. 186. *Apparatus for Testing the Conductivity of a Solution*

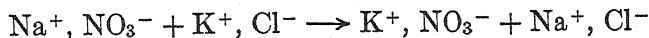
Other arguments for Arrhenius's theory. Today a great deal of accumulated evidence of various sorts can be interpreted in terms

of the Arrhenius theory, and may be said to "support" the theory. Some of this evidence relates to the effect of ions on the density, refractive index, and color of solutions; to the catalytic effect of certain ions; to the effect of ions on viscosity and solubility; to the voltages of galvanic cells; and to many other things.

The law of thermoneutrality. It has long been known that *when dilute solutions of two soluble salts are mixed, there is little or no heat change*, either evolution or absorption of heat. This generalization is known as the *law of thermoneutrality*. For example, consider the equation



According to the ionization theory the four ions Na^+ , K^+ , NO_3^- , and Cl^- , are present as such in dilute solution, both before and after mixing the two solutions:



No reaction occurs at all in dilute solution. It is only when we concentrate the solution (for example, by evaporation) that crystals of the various compounds appear. Therefore we can readily understand why, in dilute solutions, there should be little evidence of any heat of reaction.

Interpretation of electrolysis. The present idea of the mechanism of electrolysis may now be explained in terms of ions by reference to Fig. 187; the electrolysis of hydrogen chloride is used as an example. Hydrogen chloride is present in the cell largely as the ions H^+ and Cl^- . The battery *C* acts much as a pump, pumping electrons away from the anode *B* (leaving it positively charged) and

pushing them along to accumulate on the cathode *A*, which becomes negatively charged. Positive hydrogen ions (H^+) are attracted to the cathode and recover their missing electrons from it. The resulting hydrogen atoms pair up and escape as molecular hydrogen.

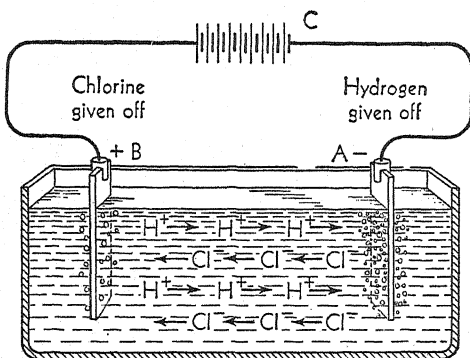


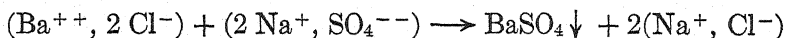
FIG. 187. A Diagram Illustrating the Theory of the Electrolysis of a Solution of Hydrogen Chloride

The negative chloride ions (Cl^-) move toward the anode, deliver to it their excess electrons, become neutral chlorine atoms, and escape as molecular chlorine gas.

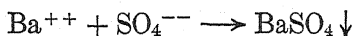
In the wire, electrons move from anode to cathode; in the solution, they move (on chloride ions) from cathode to anode.

Reactions and properties due to ions. Since a solution of an electrolyte consists of a mixture of two oppositely charged ions, the chemical behavior of such a solution will depend upon the individual ions present.

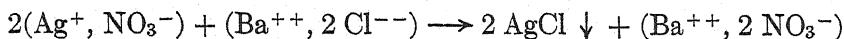
In this way, the reactions which would be expected of a solution of barium chloride, $BaCl_2$, will be those of the barium ion, Ba^{++} , and the chloride ion, Cl^- . Thus, toward any soluble sulfate a solution of barium chloride will give a precipitate characteristic of the barium ion,



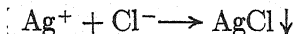
or simply



and toward a soluble silver salt, a precipitate characteristic of the chloride ion,



or essentially

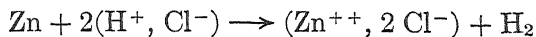


It follows, too, that a solution of any other soluble chloride will give the same reaction with solutions of silver salts, regardless of the particular cation present in the solution.

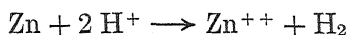
By similar reasoning we should expect that the color of a dilute solution of an electrolyte would be due to one or the other of its ions, and that the solution of any other electrolyte having this same colored ion would have the same color. Accordingly we find that dilute solu-

tions of all copper salts are pale blue, the color of the cupric ion, Cu^{++} , while those of the permanganates are bright purple, the color of the permanganate ion, MnO_4^- .

The electromotive series. We have seen that when certain metals are brought into contact with an acid solution, hydrogen ions are discharged and an equivalent weight of the metal passes into solution as ions:

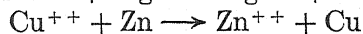
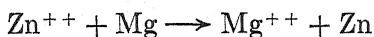


Since the chloride ions do not take part in this reaction, the equation may be written simply,



The hydrogen ions recover their missing electron from the metallic atoms, which are thus seen to have a smaller affinity for their electrons than hydrogen does.

In an entirely similar manner, there are many reactions in which one metal displaces another from the ionic condition:



The latter reaction is very striking when zinc dust is sprinkled into a solution of copper sulfate. The blue color of the solution soon disappears, and dark-brown copper powder is precipitated in place of the gray zinc. It is possible to arrange all the metals in the order in which they will displace each other in this way. Such an arrangement is known as the *electromotive series of the metals*:

Electromotive Series of the Metals

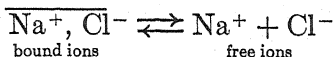
1. Lithium	7. Manganese	13. Nickel	19. Mercury
2. Potassium	8. Zinc	14. Tin	20. Silver
3. Calcium	9. Chromium	15. Lead	21. Platinum
4. Sodium	10. Iron	16. Hydrogen	22. Gold
5. Magnesium	11. Cadmium	17. Copper	
6. Aluminum	12. Cobalt	18. Arsenic, antimony, bismuth	

All the metals above a given one in the series will displace its ions from solutions, while it in turn will displace all those of lower position. The place of hydrogen in the series is most interesting. All those metals which precede it will, under favorable conditions, evolve hydrogen from dilute acids, while those which follow will not.

The electromotive series of the metals really represents the relative ease with which the various atoms give up one or more valence electrons to form *positive* ions. The atoms of lithium (the metal going into solution most readily) part with an electron most easily,

while the atoms of such metals as gold and platinum retain their normal number of electrons most tenaciously. The nonmetallic elements can be arranged in a similar series, which represents the relative ease with which they *gain an excess* electron, and so become *negative* ions.

Debye-Hückel, or interionic-attraction, theory. We have seen that X-ray studies of crystals of electrovalent compounds show these crystals to be composed wholly of ions, and it is reasonable to assume that such crystals pass into solution *as ions*. On the other hand, all the evidence on which Arrhenius based his theory goes to show that a considerable percentage of an electrolyte in solution is present in *molecular* form or at least is not in the form of free ions. Debye and Hückel reconciled these differing conclusions in this way: They assumed that most of the salts and the strong acids and strong bases are 100 per cent ionized in solution, regardless of the dilution. But their ions, some positively charged and others negatively charged, moving about in the solvent, *attract each other*, the attraction being due to electrostatic forces. These forces operating between oppositely charged ions bind the whole set into a sort of lattice, or at least bind groups of ions into clusters. This diminishes the mobility of the ions and makes it more difficult for the individual ions to act as free ions. In such solutions we may consider, then, two classes of ions — namely, those that are bound together by electrostatic forces and those that are free to move about at random. To distinguish between these two classes we may call the former *bound* ions and the latter *free* ions and express the equilibrium as follows:



The more dilute the solution, the farther apart will be the ions, and the fewer will there be of those bound together by attractive force. With increasing dilution, there will be an increasing proportion of free ions, and at a sufficiently great dilution all ions will act as free ones.

In effect, the picture offered in the Debye-Hückel theory amounts in most of its consequences *virtually* to the picture in the Arrhenius theory of only partially dissociated molecules. For the chemical behavior of ions and their physical behavior in modifying the freezing point, boiling point, and so on of a solvent depend on the extent to which they can act unhindered as free, individual particles; and their free action is hindered equally whether united in molecules or bound together in clumps by electrical attraction. We

may then continue to speak of the *degree of ionization*, meaning the proportion of *free ions* in a solution.

Other values of the Debye-Hückel theory. The theory of Arrhenius is concerned almost wholly with the *number* of ions formed by an electrolyte; the Debye-Hückel theory places stress on the *charge* of ions, as well as on the number of ions. As a consequence it throws light on some additional facts about degree of ionization.

In view of the fact that the charge on the calcium ion (Ca^{++}) is twice that on the sodium ion (Na^+), we should expect the Ca^{++} ion to attract anions more strongly than the Na^+ ion. Consequently in a solution of calcium chloride (Ca^{++} , 2Cl^-) there should be a larger proportion of bound ions (smaller degree of ionization) than in a solution of (Na^+ , Cl^-) of comparable concentration. With a solution of copper sulfate (Cu^{++} , SO_4^{--}) there should be an even greater percentage of bound ions, for *both* ions have double charges. These conclusions are borne out by the results arranged in the following table:

Table of Ionization (Free Ions) in Solutions at 18°

ACIDS (NORMAL SOLUTION*)	PER CENT	SALTS (MOLAR SOLUTION)	PER CENT
Nitric	85.0	Potassium chloride	74.2
Hydrochloric	79.0	Potassium iodide	72.7
Sulfuric	51.0	Sodium chloride	74.1
Acetic	0.3	Ammonium chloride	75.0
		Potassium nitrate	61.3
BASES (NORMAL SOLUTION)		Calcium nitrate	54.9
Potassium hydroxide	76.0	Silver nitrate	61.7
Sodium hydroxide	72.0	Potassium sulfate	59.2
Barium hydroxide	69.0	Magnesium sulfate	34.9
Ammonium hydroxide	0.3	Zinc sulfate	30.9
Calcium hydroxide (<i>N</i> /64)	90.0	Copper sulfate	30.9
(Very little soluble)		Mercury salts	Very little

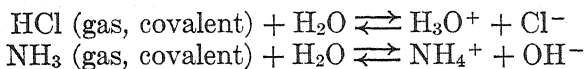
Weak and strong electrolytes. As indicated in the table, electrolytes differ greatly among themselves in their degree of ionization. Most electrolytes mentioned in the preceding pages are highly ionized in solution and are called *strong* electrolytes. This class includes nearly all salts and the more chemically active acids and bases. A large number of other compounds are known, particularly among the acids and bases, that are only slightly ionized in solution

* Normal (*N*) solutions are those which contain 1 g-equiv wt of a substance per liter of solution.

and are collectively called *weak* electrolytes. Examples of these are acetic acid and ammonium hydroxide.

Very weak electrolytes. Neither theory of ionization accounts very well for the small degree of ionization of many electrolytes — often much less than 1 per cent. There are several considerations that give a partial answer to this problem. In the first place, the distinction between a covalent and electrovalent bond is not a hard-and-fast one. A covalent compound may set up an equilibrium with an electrovalent modification which results in a very small degree of ionization.

Ionization by reaction with the solvent. Again, some covalent compounds react chemically with water to form a certain percentage, large or small, of an electrolyte. For example, we have the reactions



The first reaction is practically complete; so nearly all the HCl molecules are changed into ions, and the solution acts as a *strong* electrolyte. The second reaction reaches an equilibrium involving only a small percentage of ammonium and hydroxyl ions result; so the solution acts as a *weak* electrolyte. The ion H_3O^+ (called *hydronium ion*) occupies an important position in the Brönsted theory of acids and bases soon to be discussed (pp. 303–305).

Questions

1. If crystals of an electrovalent compound (such as Na^+ , Cl^-) are built up of ions, why are they not good conductors of electricity?
2. During the electrolysis of a solution of hydrogen chloride, why does hydrogen come off at the cathode only, and not at all points between the anode and the cathode?
3. In the electrolysis of water (p. 88), (a) why is sulfuric acid added to the water? (b) From what source do the hydrogen and the oxygen come? (c) Is sulfuric acid used up in the process of electrolysis? (d) How do you account for the evolution of oxygen?
4. Under ordinary conditions electrical energy is used up in the process of electrolysis. (a) Is it used up in parting the electrolyte into ions? (b) Can you suggest other ways?
5. Iron (Fe) forms two chlorides, one in which the iron is bivalent and another in which it is trivalent. (a) Write the formulas for the two compounds. (b) Write the equations for the ionization of each when dissolved in water. (c) Would the color of the two solutions necessarily be the same?

6. What position should you expect the metals found free in nature to occupy in the electromotive series of the metals?

7. What takes place in each of the following cases: (a) an iron nail in a solution of copper sulfate; (b) a strip of tin in a solution of mercuric chloride (HgCl_2); (c) a copper penny in a solution of mercuric sulfate (HgSO_4); (d) a silver coin in a solution of zinc sulfate?

Problems

1. Suppose you were to add 50 g of iron to an aqueous solution of 100 g of copper sulfate. (a) When the reaction was completed, what products would be present? (b) Calculate the weight of each.

2. If 0.2 g-mol. wt of cane sugar is dissolved in 1000 g of water, what will be (a) the freezing point of the solution; (b) the boiling point?

3. What will be the freezing point of a solution of 0.2 g-mol. wt of sodium chloride in 1000 g of water if the sodium chloride is 90 per cent ionized?

4. What will be the boiling point of a solution of 20 g of sodium chloride in 1000 g of water if the sodium chloride is 100 per cent ionized?

5. (a) What would be the freezing point of 1 g-mol. wt of copper sulfate (CuSO_4) in 1000 g of water (see table on page 279)? (b) Why should this salt be so low in degree of ionization?

Reading References

ARRHENIUS. "Electrolytic Dissociation," *Journal American Chemical Society*, Vol. XXXIV, pp. 353-364. An address by Arrhenius on the occasion of his visit to the United States, in which he tells the story of the development of his theory.

FRENCH. *The Drama of Chemistry*. See pages 54-61 for the theory of ions.

JAFFE. *Crucibles*. Chapter XII gives a very interesting sketch of the life of Arrhenius and his development of the theory of electrolytic dissociation.

VAN'T HOFF and ARRHENIUS. *The Foundations of the Theory of Dilute Solutions*, Alembic Club Reprints, No. 19.

The Chemistry of Common Salt

Occurrence of sodium chloride (salt). Sodium chloride, NaCl , is very widely distributed in nature. Thick strata, evidently formed by the evaporation of salt water, are found in many places. In the United States the most important localities are Michigan, New York, and Ohio. Sometimes the salt is mined as *rock salt*; very often, however, a strong brine is pumped from deep wells driven into the salt deposit and the brine is then evaporated in large pans until the salt crystallizes. In other places salt is recovered by the evaporation of sea water.

Salt crystals form small cubes, are anhydrous, and melt at 804° . Pure salt does not absorb moisture from the air unless the humidity of the air is at least 75 per cent; but table salt becomes moist in much drier air because of impurities. Salt is essential for animal life, and it is said that the average person consumes about 30 lb annually. It is the source of the hydrochloric acid that constitutes from 0.4 to 0.5 per cent of the human gastric juice.

Industrially salt is used not only as the source of both sodium and chlorine themselves, but also in the preparation of nearly all substances that contain either of these elements. These include many products of the highest importance to civilization, such as soap, paper, glass, rayon, hydrochloric acid, sodium carbonate, and bleaching powder. To meet these demands about 8,000,000 tons of salt are produced annually in the United States.

Electrolysis of sodium chloride. Sodium chloride is an electrovalent compound (Na^+ , Cl^-); and when its crystals are melted or dissolved in water, it is an electrolyte. Under either of these conditions the ions of salt are free to move about, and in an electric field the Na^+ ions move toward the cathode and the Cl^- ions toward the anode. Upon reaching the electrodes the ions lose their charges, and the reactions that then take place depend on the conditions of the electrolysis.

1. **Electrolysis of melted salt.** When an electric current passes through liquid (melted) sodium chloride, the sodium ions (Na^+) on arriving at the cathode recover their missing electrons from the

negative cathode and become neutral atoms of the metal sodium. The chlorine ions (Cl^-) move toward the anode, where each surrenders its extra electron and becomes a neutral atom of chlorine. If the material of the anode is not acted on by atomic chlorine, the atoms combine in pairs to form chlorine molecules, Cl_2 . These reactions are represented below; the symbol e^- is used to represent an electron.

Cathode reaction: $\text{Na}^+ + e^- \longrightarrow \text{Na}$ (silvery metal)

Anode reaction: $2 \text{Cl}^- - 2 e^- \longrightarrow \text{Cl}_2$ (greenish-yellow gas)

At the cathode sodium ions are reduced to sodium atoms (gain of electrons). At the anode chlorine ions are oxidized to chlorine atoms (loss of electrons). The method above serves for the commercial production of sodium (Fig. 188).

2. *Electrolysis of dissolved salt.*

In a water *solution* of salt, chlorine is liberated at the anode, as with melted salt; but at the cathode hydrogen is evolved in quantities equivalent to those of the chlorine. We might have expected the sodium to be liberated rather than the hydrogen. The explanation must be found in the fact that sodium gives up its valence electron to become an ion more readily than hydrogen; so the hydrogen ion from water more readily recovers its valence electron from the cathode than the sodium ion. The discharge of each hydrogen ion leaves a hydroxyl ion (OH^-) to balance each sodium ion; in other words, the ions of sodium hydroxide remain in solution. Practically all the chlorine and much of the sodium hydroxide used commercially are prepared in this way.

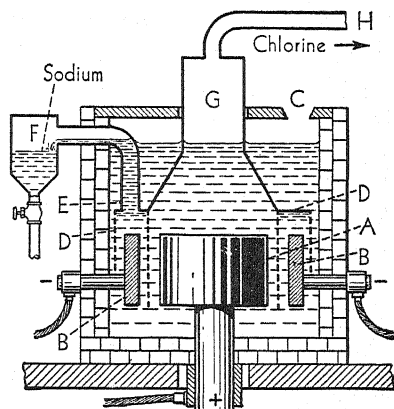


FIG. 188. *Diagram of the Downs Cell for the Production of Sodium*

The essential parts of the Downs cell are as follows: *A* represents the anode (made of graphite), and *B*, *B*, an annular iron or steel cathode, which is surrounded by the annular compartment *D*, *D*. The melted sodium chloride is admitted at *C*. When the current is connected, the sodium liberated at the cathode *B*, *B*, being very light, rises to the top of the compartment, flows upward through the tube *E*, and over into the container *F*, from which it is withdrawn from time to time. The chlorine escaping from the anode *A* rises in the dome *G* and escapes through the pipe *H*.



FIG. 189. *Karl Wilhelm Scheele*
(1742–1786)

A Swedish chemist and one of the greatest experimenters of all times. He discovered oxygen, ammonia, and hydrochloric acid independently of Priestley. He also discovered chlorine, as well as the very poisonous gases arsine and hydrocyanic acid. Among the organic compounds first prepared by Scheele are glycerin, milk sugar, lactic acid, gallic acid, citric acid, oxalic acid, and tartaric acid. He was one of the ablest as well as one of the latest defenders of the phlogiston theory of combustion



FIG. 190. *Sir Humphry Davy*
(1778–1829)

Appointed director of the Royal Institution of London when only twenty-two years of age. Trained Michael Faraday as his assistant. The first to isolate the metals sodium and potassium and to prove that chlorine is an element. The inventor of the miner's safety lamp. Reproduced from a painting by Sir Thomas Lawrence, by permission of the Royal Society, London

CHLORINE

History and occurrence of chlorine. The element chlorine was first isolated by Scheele (Fig. 189) in 1774. Because of its activity, it does not occur free in nature. Scheele obtained it by liberating it from hydrochloric acid by the action of manganese dioxide, a method of preparation which is still used. For years the element was regarded as a compound of hydrochloric acid with oxygen until, in 1810, the English chemist Davy (Fig. 190) proved its elementary character, and because of its color named it *chlorine*, from a Greek word meaning "greenish yellow."

The Vorce cell for the production of chlorine. Several types of cells are in use in the United States for the production of chlorine,

each designated by the name of its inventor. In obtaining chlorine (and sodium hydroxide) by electrolysis of a salt solution, the chlorine

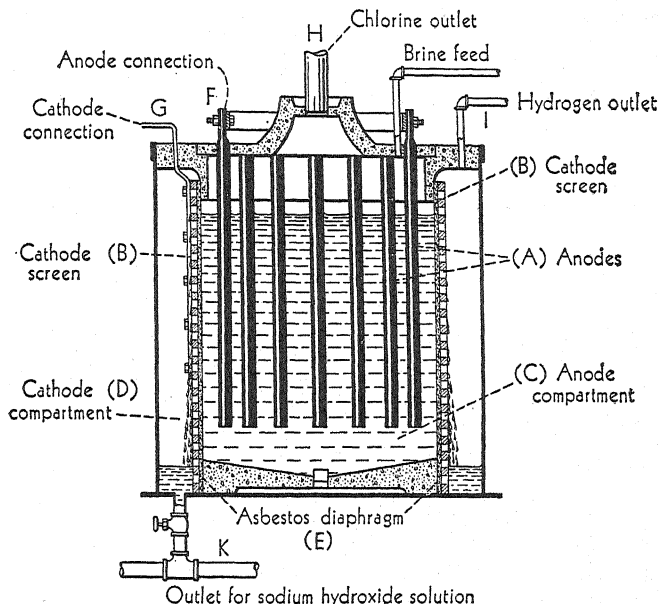


FIG. 191. *The Vorce Cell for Producing Chlorine*

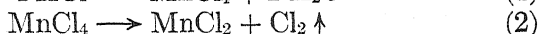
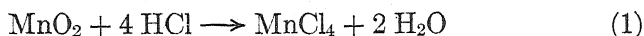
The salt brine is placed in a large cylindrical container and renewed from time to time through the brine feed. A number of graphite anodes *A* are dipped into the brine. The cathode of wire screening *B* surrounds the group of anodes in the form of a hollow cylinder, and is separated from the electrolyte by an asbestos diaphragm *E* to prevent mechanical stirring of the liquid. Hydrogen is evolved at the cathode and escapes through the hydrogen outlet *I*. Chlorine is evolved at the anode surfaces, collects under the domelike top, and escapes through the chlorine outlet *H*. The sodium hydroxide formed in the electrolysis is drawn off at the bottom *K* of the cell

evolved at the anode must be prevented from acting on the sodium hydroxide formed at the cathode. In the Vorce cell (Fig. 191) this is done by separating the anode and cathode compartments by a porous diaphragm. Under ordinary conditions each cell produces about 72 lb of sodium hydroxide and 64 lb of chlorine every twenty-four hours. The hydrogen evolved in the process is used in preparing hydrochloric acid and ammonia. The chlorine is used directly for bleaching, or is pumped into strong steel containers ranging in size from small flasks to tank cars. Sodium hydroxide is recovered from the cathode compartment.

The electrolytic method for preparing chlorine possesses the following advantages: (1) sodium chloride is cheap; (2) in addition

to chlorine, sodium hydroxide, for which there is great demand, is formed in the process. The chief item of cost is the generation of electrical energy, so that factories for the production of chlorine are likely to be located at points where water power can be used to advantage, as at Niagara Falls.

Laboratory preparation of chlorine. On a small scale in the laboratory chlorine is prepared by the oxidation of hydrochloric acid. This can be done by treating manganese dioxide, MnO_2 (pyrolusite), with hydrochloric acid. The reaction probably takes place in two stages, as indicated by the equations



By canceling the formula for the compound (MnCl_4) formed in equation (1) and used up in equation (2), these two equations may be combined into the following single equation:

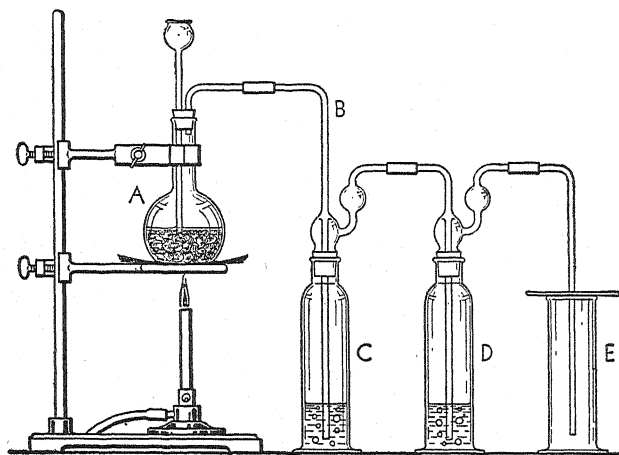
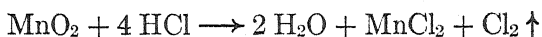


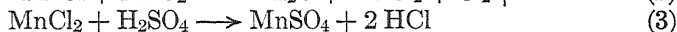
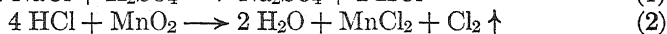
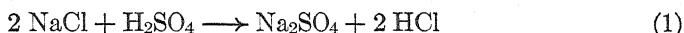
FIG. 192. *Diagram of Apparatus Used in the Laboratory for Preparing Chlorine by the Action of Hydrochloric Acid on Manganese Dioxide*

The manganese drops from a valence of 4 to 2 and so is reduced (gains electrons), while half of the chlorine ions each lose one electron (are oxidized). Many other oxidizing agents oxidize hydrochloric acid with the production of chlorine.

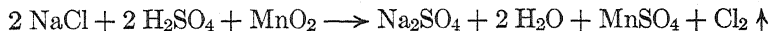
Experimental details. The manganese dioxide and hydrochloric acid are placed in the flask A (Fig. 192) and thoroughly mixed. A gentle heat

is then applied to the flask. Chlorine is evolved and, escaping through the tube *B*, bubbles through the water in bottle *C* (which dissolves any hydrochloric acid carried over with it) and finally through some sulfuric acid in bottle *D* (which removes any moisture present). Since the gas is fairly soluble in water, it is collected by displacing the air in bottles or cylinders *E*. Because of the poisonous character of chlorine, its preparation should be carried on in a well-ventilated hood.

Since sodium chloride and sulfuric acid act upon each other to form hydrogen chloride, it is often more convenient to substitute a mixture of these two compounds for the hydrochloric acid. The equations for the reactions involved are as follows:



The three equations may be combined in a single one as follows:



Properties of chlorine. Chlorine is a greenish-yellow gas and possesses a peculiar suffocating odor. It is 2.49 times as heavy as air, and under ordinary conditions 1 volume of water dissolves about 2.5 volumes of the gas. At ordinary temperatures (18°) it is liquefied by a pressure of 16.5 atm. In commercial containers (iron cylinders or tank cars) it is largely in the liquid state. Liquid chlorine is yellowish in color, boils at -34.6° under atmospheric pressure, and freezes at -101.6° . Its critical temperature is 144° . When inhaled in small quantities, chlorine produces the symptoms of a hard cold, and in larger quantities has serious and even fatal effects.

Chemical conduct. At ordinary temperatures chlorine is one of the most active of all the elements. The compounds formed by its union with any other element are called *chlorides*.

1. **Action upon other elements.** Nearly all the metals combine directly with chlorine, especially when heated or powdered. A strip of copper foil, heated to redness and immediately dropped into chlorine, burns with incandescence. Sodium burns brilliantly when

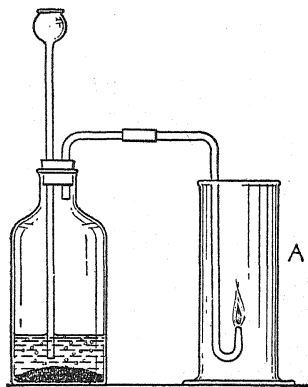


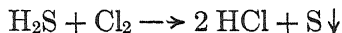
FIG. 193. *Hydrogen Burning in an Atmosphere of Chlorine*

heated strongly in moist chlorine. Gold and silver are quickly tarnished by the gas, and even platinum is readily attacked by it.

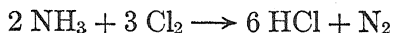
Chlorine has likewise a strong affinity for most of the nonmetals. Phosphorus, sulfur, antimony, and arsenic burn in a current of the gas.

Chlorine unites readily with hydrogen, forming hydrogen chloride. A jet of hydrogen burning in the air continues to burn when introduced into a jar *A* of chlorine, giving a somewhat luminous flame (Fig. 193). A mixture of the two gases explodes violently either when heated or when exposed to bright sunlight.

2. Action upon compounds of hydrogen. Not only will chlorine combine directly with free hydrogen, but it will remove hydrogen from some of its compounds. Thus, when chlorine is passed into an aqueous solution of hydrogen sulfide, sulfur is precipitated and hydrochloric acid formed, as expressed in the following equation:



With ammonia the action is similar:



Under certain conditions the reaction with ammonia yields a very explosive, oily liquid known as nitrogen trichloride (NCl_3). The strong affinity of chlorine for hydrogen is very strikingly shown by its action upon turpentine ($\text{C}_{10}\text{H}_{16}$). When a strip of paper moistened with warm turpentine is placed in a jar of the gas, the chlorine unites with the hydrogen of the turpentine with evolution of light, forming hydrogen chloride, while a black deposit of carbon remains.

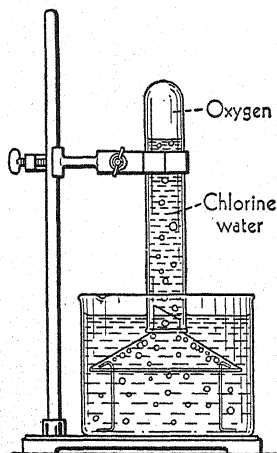
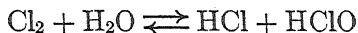


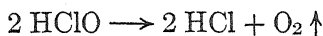
FIG. 194. Action of Chlorine on Water in Bright Sunlight

3. Action upon water. At ordinary temperature and pressure one volume of water dissolves a little over two volumes of chlorine, and the solution is called *chlorine water*. Slightly above the freezing point of water a solid hydrate separates which has the composition $\text{Cl}_2 \cdot 8 \text{H}_2\text{O}$. When warmed, this compound dissociates into its constituents; and it was by taking advantage of these properties that Faraday in 1823 first liquefied chlorine (Fig. 82, p. 122).

The chlorine in solution slowly reacts with the water to form small concentrations of hydrochloric acid and a compound called hypochlorous acid (HClO), but an equilibrium is soon reached :



The hypochlorous acid decomposes into hydrochloric acid and oxygen, slowly in diffused light but rapidly in bright sunlight ; and the final result is a solution of hydrogen chloride and evolved oxygen :



The decomposition of water through the action of chlorine is also greatly increased in the presence of some substance which combines with the oxygen as fast as it is set free. Consequently a solution of chlorine in water is a good oxidizing agent.

Experiment. The effect of sunlight in increasing the action of chlorine upon water may be shown in the following way : If a long tube of rather large diameter is filled with a saturated solution of chlorine in water and inverted in a vessel of the same solution (Fig. 194), and the apparatus is placed in bright sunlight, bubbles of gas will soon be seen to rise through the solution and collect in the tube. An examination of this gas will show that it is oxygen.

4. Action as a germicide. Chlorine has marked *germicidal properties*, and both the free element and the compounds from which it is easily liberated are used as disinfectants and antiseptics. For this reason free chlorine is widely used in the purification of city water supplies.

5. Action of moist chlorine on colored materials ; bleaching. Chlorine water is a powerful bleaching agent. Strips of highly colored cloth, when moistened with water and placed in jars of chlorine, rapidly lose their color. The presence of water is essential to the change, as may be shown by placing strips of the dry cloth in chlorine from which the moisture has been removed by bubbling it through sulfuric acid (Fig. 192). Under these conditions the color of the cloth remains unchanged or nearly so.

The bleaching action of chlorine is in reality due to the oxidizing action of hypochlorous acid, as explained in No. 3 above, the oxygen reacting with the color substance of the cloth to form colorless compounds. Chlorine has no bleaching action on substances that are not easily oxidized, such as carbon, and so does not affect printer's ink. It should not be used for bleaching certain substances, such as silk, since it injures the fabric.

Bleaching is an important process in connection with many industries. Thus, the various kinds of fabrics woven from vegetable fibers, such as flax and cotton, are always more or less colored, and bleaching is necessary if a white fabric is desired. This was formerly accomplished by spreading the cloth on plots of grass and exposing it to air and sunlight, but the process was very slow. The same results are now obtained in a short time by the use of chlorine.

The nascent state. The student may well ask, "Why does the oxygen from hypochlorous acid have a rapid bleaching effect, while free oxygen itself bleaches colors very slowly?" The simplest answer is that at the instant oxygen is set free from a compound, it consists of free *atoms*, whereas oxygen gas is made up of oxygen *molecules*. The free atoms are more active than the molecules, as is evident from the fact that work must be done to part the molecules into atoms. The parted atoms then have additional energy and on this account enter into reactions more rapidly than molecules. To distinguish between the energetic uncombined atoms and the molecules, we say that the atoms at the instant of liberation from compounds are in the *nascent state*. The word *nascent* means "newborn."

Uses. The normal production of chlorine in the United States amounts to between 900 and 1000 tons daily. Most of this is used either in bleaching fabrics or in the bleaching of wood pulp from which paper is made. It is also used in the purification of water and in making *bleaching powder* and such compounds as chloroform (CHCl_3), carbon tetrachloride (CCl_4), and various antiseptics and disinfectants.

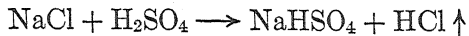
HYDROGEN CHLORIDE AND HYDROCHLORIC ACID

Introductory. With hydrogen, chlorine forms the simple gaseous compound *hydrogen chloride* (HCl). This gas is very soluble in water, and the resulting solution is called *hydrochloric acid*. This distinction between the compound itself and its solution in water is desirable, though it is not always observed in chemical literature.

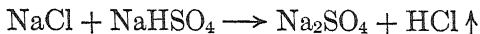
Preparation of hydrogen chloride and hydrochloric acid. Two general methods for preparing hydrogen chloride will be described. To prepare hydrochloric acid, it is only necessary to bring the chloride into solution in water.

1. **By the direct combination of hydrogen and chlorine.** These two gases readily combine, forming hydrogen chloride (p. 288). Since both the hydrogen and chlorine are obtained in quantities in the electrolysis of a solution of sodium chloride, this method is used to a limited extent in the preparation of hydrogen chloride on an industrial scale.

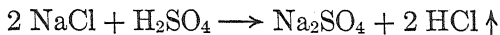
2. *By the action of concentrated sulfuric acid upon chlorides of metals.* Because of its low cost sodium chloride is always used for this purpose. The reaction takes place in two steps. The first,



takes place upon bringing the salt and sulfuric acid together at ordinary temperatures. The second requires heating and is as follows:



By combining the two equations the following is obtained:



It will be observed that in this reaction sodium sulfate is formed along with hydrogen chloride. Since there is a considerable use for sodium sulfate, this method of preparation has an advantage in that both compounds formed are of value. The first reaction is a convenient one for the preparation of hydrogen chloride in the laboratory.

Laboratory preparation. Sodium chloride is placed in the flask A (Fig. 195), which is fitted with a funnel tube and an exit tube; sulfuric acid of the proper concentration is added, and the flask is gently warmed. Hydrogen chloride is evolved, since it is insoluble in *concentrated sulfuric acid*, and is collected by displacement of air, as in the preparation of chlorine. To prepare a solution of the gas, the end of the exit tube is fixed just above the level of some water contained in a cylinder B. Since the gas is extremely soluble in water, it is absorbed as fast as it escapes from the tube. Care must be taken not to have the end of the exit tube dip below the surface of the water, since the solubility of the gas is so great that the water would suck back into the generating flask and cause trouble.

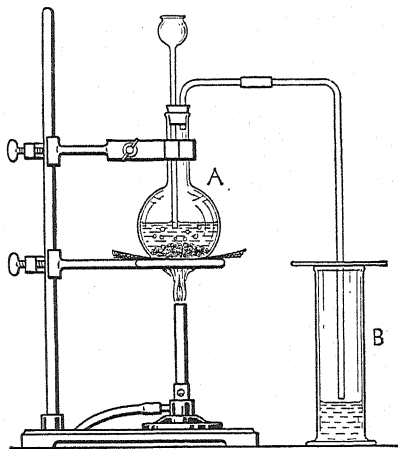


FIG. 195. *The Preparation of a Solution of Hydrogen Chloride*

If the sulfuric acid is added, not to the solid sodium chloride but to an aqueous solution of the salt, there is no very marked action. The hydrogen chloride formed is very soluble in water and so does not escape from the solution; consequently a state of equilibrium is soon reached among the ions of the four substances represented in the equation.

Liberation of hydrogen chloride from its solution. The pure hydrogen chloride can easily be regained from its concentrated aqueous solution by

the addition of sulfuric acid, which diminishes the solubility of the hydrogen chloride. This is a very convenient method for obtaining pure gaseous hydrogen chloride when a limited supply of it is desired in the laboratory. The concentrated solution is placed in *A* (Fig. 196), and the flask is connected with the bottle *B*, which contains sulfuric acid for drying the gas. This bottle is fitted with stopper and tubes, as shown in the diagram. The glass tube leading from the bottle *B* to the bottom of the cylinder *E* passes through a perforated cardboard or glass plate *C*, which rests lightly on the top of the cylinder. Sulfuric acid is now added,

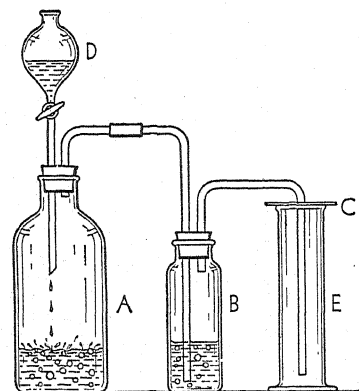


FIG. 196. *Liberating Hydrogen Chloride from Its Solution*

drop by drop, from the separatory funnel *D* to the concentrated solution in *A*. The hydrogen chloride is rapidly evolved and is collected in the cylinder *E*, as shown in the figure.

By-products. In the preparation of any given substance it usually happens that other compounds are formed. These are called *by-products*. Thus sodium sulfate is a by-product in the manufacture of hydrochloric acid (p. 291). It is evident that the cost of the manufacture of any substance can be decreased to the extent to which the by-products can be utilized. Indeed, the demand for the by-product may become so great that it really comes to be the main product. The success of a process often depends upon the value of its by-products.

Properties of hydrogen chloride. Hydrogen chloride, a colorless gas, is 1.26 times as heavy as air. When inhaled it has an irritating and suffocating effect. At 0° it is condensed to the liquid state by a pressure of 28 atm. This liquid is colorless, boils at -85° , and solidifies at -111° . *It does not conduct electricity, has no action upon metals, and in general is inactive.* Hydrogen chloride is very soluble in water, 1 volume of the latter under standard conditions dissolving 506 volumes of the gas. The density of its aqueous solutions increases with the concentration of the gas, as is shown in the following table, which gives the percentage *by weight* of hydrogen chloride present in solutions of various densities at 15° :

PER CENT OF HCl	DENSITY	PER CENT OF HCl	DENSITY	PER CENT OF HCl	DENSITY
5.69	1.0284	20.04	1.1006	35.02	1.1779
10.17	1.0507	25.06	1.1265	40.09	1.2013
15.22	1.0761	30.00	1.1526	43.40	1.2134

A solution of hydrogen chloride in water, containing 20.24 per cent of the gas, has a constant boiling point (110°) at a pressure of 760 mm (p. 257). Solutions more concentrated lose hydrogen chloride, while more dilute solutions lose water, until the above concentration is reached, when they boil with unchanged concentration.

Solubility of hydrogen chloride. The extreme solubility of hydrogen chloride in water may be shown as follows: A perfectly dry flask A (Fig. 197) is filled with hydrogen chloride. This flask is connected, by means of a glass tube, with a similar flask B, which is nearly filled with water, as shown in the figure. The end of the tube opening into flask A is drawn out to a rather fine jet. By blowing into the tube C, a few drops of water are forced into A. Some of the hydrogen chloride at once dissolves, thus diminishing the pressure inside the flask. The water then flows continuously from B into A, until practically all the hydrogen chloride is absorbed. It is evident that the connections must be airtight.

Properties of hydrochloric acid. When pure materials are used, the solution of hydrogen chloride in water (hydrochloric acid) is a colorless liquid. The commercial acid, often colored yellow by impurities, is frequently called *muratic acid*. While hydrogen chloride itself has but little chemical activity, its *aqueous solution* has marked properties, which, for the most part, are those common to all compounds known as *acids*. These properties are due to the formation of *hydrogen ions* in solution, and may be summarized as follows:

1. **Taste.** The dilute acid has a sour taste like that of vinegar or of lemons or of many unripe fruits.

2. **Action on colored compounds.** Hydrochloric acid alters the color of many compounds (*indicators*). Thus it readily changes the

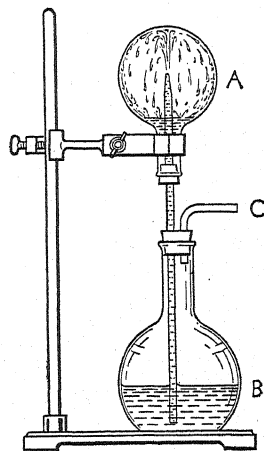
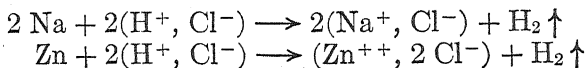


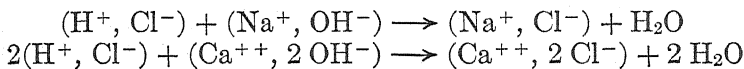
FIG. 197. Apparatus for Showing the Extreme Solubility of Hydrogen Chloride in Water

blue color of *litmus* to red, and the yellow color of *methyl orange* to pink.

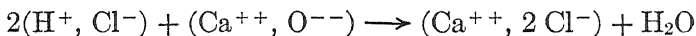
3. *Action upon metals.* Many of the metals, such as sodium, iron, tin, and zinc, dissolve in hydrochloric acid, forming chlorides of the metals and liberating hydrogen :



4. *Action upon the hydroxides of the metals.* When hydrochloric acid and the hydroxide of a metal are brought together, the hydrogen of the acid and the metal of the hydroxide exchange places, forming a chloride of the metal and water :



Similarly, the acid acts upon the oxides of the metals :



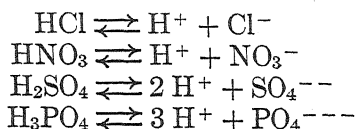
The chlorides. The compounds of chlorine with a metal (see 3 and 4 above) are known as *chlorides*, and constitute an extremely important group of compounds. Some of them, as sodium chloride and potassium chloride, are found in nature. A number of the metals, including copper, mercury, and tin, combine with different percentages of chlorine, and thus form two chlorides. Nearly all the chlorides of the metals are solids; and, with the exception of those of silver, mercury (mercurous), and lead, the chlorides of all the common metals are soluble in water.

Some of the more important chlorides are the following: *sodium chloride* (common salt) (NaCl); *potassium chloride* (KCl); *mercurous chloride* (calomel) (Hg_2Cl_2); *mercuric chloride* (corrosive sublimate) (HgCl_2); *ferric chloride* (FeCl_3); *barium chloride* (BaCl_2); *calcium chloride* (CaCl_2); *zinc chloride* (ZnCl_2).

Acids. In addition to hydrochloric acid, some familiar acids are nitric, sulfuric, and phosphoric acids. In Chapter 11 a number of acids were described as resulting from the action of nonmetallic oxides on water (p. 185), and here we meet with hydrochloric acid, which contains no oxygen. What properties do all these compounds called acids have in common which serve to group them together as acids? Certainly it is important to arrive at a definition that will characterize acids clearly as a class.

In a general way, like hydrochloric acid, all acids contain hydrogen, have a more or less sour taste, change the color of indicators, and

act on bases to form salts. A much more definite characteristic is that all acids give hydrogen ions in solution in water. Indeed, we can reverse this statement and reach a satisfactory definition of an acid as follows: *An acid is any compound that gives hydrogen ions (H^+) in a solution.* This definition is illustrated in the equations



However, in addition to the properties held in common, acids have other properties, which may vary widely in individual cases. These properties, specific for each acid, are due to the anion present and to the *undissociated* molecules.

The available hydrogen ions of an acid. The molecules of various acids are capable of giving different numbers of free hydrogen ions in solution. The number given by a molecule of a specified acid is called the *basicity* of the acid. For example, HCl is a monohydrogen (monobasic) acid; H_2SO_4 is a dihydrogen (dibasic) acid; H_3PO_4 is a trihydrogen (tribasic) acid.

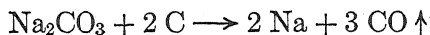
The formulas of some acids, such as acetic acid ($C_2H_4O_2$) and tartaric acid ($C_4H_6O_6$), would apparently indicate a still higher basicity; but experiment shows that in the former acid only one hydrogen atom may be replaced by metals, and in the latter only two. On this account the formulas are usually written $H \cdot C_2H_3O_2$ and $H_2 \cdot C_4H_4O_6$.

SODIUM

History. The isolation of sodium dates back to the year 1807. At that time the compounds now known as sodium hydroxide and potassium hydroxide were well known and were called *fixed alkalies*, but they were regarded as elementary in character. In 1807 Sir Humphry Davy (Fig. 190), while studying the effect of the electric current upon various substances, succeeded in decomposing these fixed alkalies, and thus obtained metallic sodium and potassium.

Davy announced his discovery in a letter to a friend, as follows: "I have decomposed and recomposed the fixed alkalies and discovered their bases to be two new inflammable substances very like metals; but one of them lighter than ether and infinitely combustible. So that there are two bodies decomposed and two new elementary bodies found."

Preparation. For many years the most economical method known for preparing sodium was the reduction of its carbonate by carbon:



This process was a difficult one to carry out and was displaced by the electrolysis of the melted hydroxide. Still more recently melted sodium chloride has been substituted for the hydroxide, and all the sodium now produced in the United States is prepared in this way.

Properties and uses. Sodium is a soft, silver-white metal. It has a density of only 0.97, and is one of the few metals that are not only lighter than water but also melt below the boiling point of water. It is very active, combining with most of the nonmetallic elements such as oxygen and chlorine. It decomposes water (p. 103) with the liberation of hydrogen. When heated in a colorless flame, sodium, as well as most of its compounds, volatilizes and colors the flame yellow — a property often used as a test for the presence of the element.

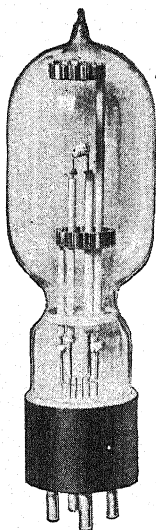


FIG. 198. A Sodium-Vapor Lamp

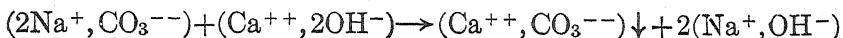
Owing to the cost of its preparation, sodium is much more expensive than the common metals, such as iron, lead, and copper. If it were sold by volume instead of weight, it would be one of the cheapest of metals. Its chief uses are in the preparation of certain compounds of the metal, such as sodium cyanide and sodium peroxide, and in the preparation of other compounds that contain no sodium, such as some of the dyes and lead tetraethyl — a constituent of the so-called "ethyl gasoline," used largely as a motor fuel. It is used in certain metallurgical processes, such as removing oxygen from silver. The sodium-vapor lamp consists of small amounts of sodium and neon in a sealed vacuum tube. As a light for roadways it promises much for the future because of the low cost of operation and its effectiveness as an illuminant (Fig. 198).

SODIUM HYDROXIDE AND BASES

Compounds of sodium. Sodium forms many useful compounds. Sodium hydroxide is a typical member of that important class of compounds known as *bases*. It is desirable to study its properties here; other compounds of sodium will be discussed later.

Sodium hydroxide (caustic soda) (NaOH). This compound is prepared on a large scale by two general processes.

1. *Action of calcium hydroxide upon sodium carbonate.* This process consists in treating calcium hydroxide suspended in water with a solution of sodium carbonate. The reaction takes place in accordance with the following equation :



The calcium hydroxide is only slightly soluble in water (about 1.6 g in 1000 cc at ordinary temperatures), but more so than the calcium carbonate. As fast as the dissolved hydroxide acts with the sodium carbonate, more of it passes into solution to continue the reaction. The calcium carbonate separates as fast as formed, and when the reaction is complete it is removed by filtration. The sodium hydroxide dissolved in the filtrate is obtained by evaporation.

2. *Electrolytic methods.* We have seen that an electric current passed through a solution of sodium chloride produces both chlorine and sodium hydroxide (p. 285), and that this process constitutes an important source of sodium hydroxide, as well as of chlorine. It is not practicable to decompose *all* the sodium chloride by electrolysis, so that the resulting solution contains both sodium chloride and sodium hydroxide. The chloride is much less soluble than the hydroxide; and when the solution is partially evaporated, the chloride separates, leaving a nearly pure solution of hydroxide. This is evaporated to dryness, and the sodium hydroxide is melted to drive off all the water. As it cools, the product solidifies as a white solid and is sold in this form.

The product prepared by either of the above methods is never pure. If desired, it may be further purified by treatment with alcohol, which dissolves the sodium hydroxide but only small amounts of the impurities. Perfectly pure sodium hydroxide may best be obtained by the action of sodium on water and the evaporation of the resulting solution.

Properties of sodium hydroxide. This compound is a white, crystalline, brittle solid. For laboratory purposes it is ordinarily sold as sticks, small pellets, or white flakes. It is often called *caustic soda*. As this name indicates, it is a corrosive substance and has a strong disintegrating action upon both animal and vegetable tissues. Exposed to the air, it absorbs both moisture and carbon dioxide and is changed into sodium carbonate. It is extremely soluble in water, and a great deal of heat is liberated in the process of solution. Its solution has a soapy feel and a strong cleansing action.

Production and uses of sodium hydroxide. About 800,000 tons of sodium hydroxide are produced annually in the United States, approximately one third of which is prepared by the electrolytic process. The compound is used in many chemical industries. Some idea of its importance can be gained from the fact that it is used in the manufacture of most kinds of hard soaps. Large quantities are also used in the manufacture of rayon and various chemicals, in the refining of petroleum, and in preparing wood pulp from which paper is made.

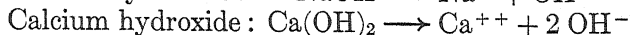
Significance of the terms *commercial* and *chemically pure*. Most compounds when prepared on a large scale contain varying amounts of impurities consisting of the substances used in the preparation of the compounds. These impure compounds are designated as *commercial* products. Commercial sodium hydroxide may contain 10 per cent or more of other ingredients. For many uses the presence of a limited amount of impurities makes no difference; and for such purposes commercial grades are used, since they are much cheaper. On the other hand, certain uses require a pure substance, and this necessitates the removal of the impurities. The purified compounds are known as *chemically pure*, or simply as C.P., to distinguish them from commercial products. The removal of impurities is often an expensive process; so the C.P. product is always the more costly. For example, C.P. sulfuric acid costs two or three times as much as the commercial grade.

The bases. The hydroxides of the various metals, including sodium hydroxide (NaOH), have many properties in common and as a group are called *bases*. Many hydroxides are insoluble in water; all the soluble ones are white solids. The very soluble bases sodium hydroxide (NaOH) and potassium hydroxide (KOH) are often called *alkalies*. In Chapter 11 bases were described as formed by the action of a metallic oxide on water (p. 185), but there are other ways in which they can be obtained, as we have seen to be true of sodium hydroxide.

There are a great many bases, and it is of importance to learn their characteristics as a class of compounds. In general, their solutions (1) taste bitter rather than sour; (2) feel soapy; and (3) reverse the color changes produced in indicators by acids—for example, they turn red litmus blue.

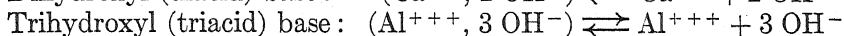
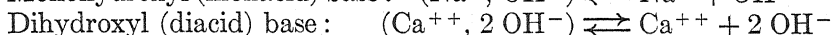
The most distinctive property of bases as a class of compounds is that they all contain hydroxyl groups, OH , and in water solution all give *hydroxyl ions*, (OH^-). Because of this property we can frame the definition *A base is any compound that gives hydroxyl ions*

in solution. The hydroxides (bases) ionize as follows :

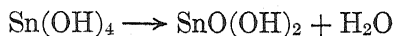


As in the case of acids, each base has individual properties as well, owing to the cation present and to the nonionized molecules of the base.

The available hydroxyl ions of a base. The molecules of the hydroxide of a univalent metal contain only one hydroxyl (OH^-) group; those of a divalent metal two hydroxyl groups; those of a trivalent metal three. These facts are sometimes indicated by the phrase *acidity of a base*, meaning the number of hydroxyl groups in the molecule and present as free ions in solution, thus :

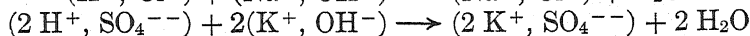
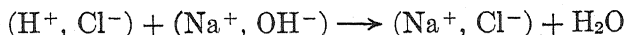


There are a few quadracid bases, such as stannic hydroxide (Sn(OH)_4); but for the most part these lose a molecule of water and act as dihydroxyl bases :

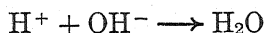


NEUTRALIZATION AND SALTS

Neutralization. If we start with a solution of an acid made red with a little litmus (p. 293), and carefully add to it a solution of a base until the red color *just* turns to blue, the resulting solution has properties that are those of neither an acid nor of a base. The base has *neutralized* the acid, and the reaction is called *neutralization*. An examination of the reaction shows that the hydrogen ions of the acid have combined with the hydroxyl ions of the base to form molecules of (covalent) water :

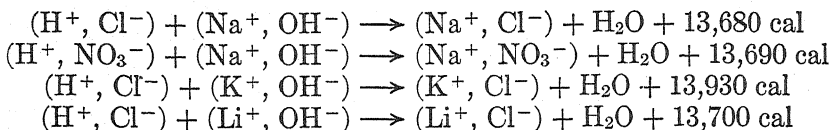


Canceling the ions common to both sides of the equations, we get



Neutralization may be defined as the union in equivalent quantities of the hydrogen ions of an acid with the hydroxyl ions of a base to form water molecules.

If the formation of water from its two ions is the only reaction taking place in neutralization in moderately dilute solution, then the heat of all such reactions should be the same. That this is so is indicated from the equations



The constant heat of neutralization reactions (approximately 13,780 cal) is the heat of formation of water by the union of a gram-equivalent of hydrogen ions with a gram-equivalent of hydroxyl ions.

Neutralization a definite act. If two solutions, one of a base and the other of an acid, are prepared, experiment has shown that a given volume of the acid solution will invariably require a perfectly definite volume of the base for its neutralization.

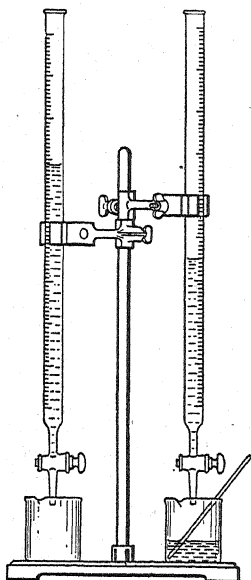


FIG. 199. *Apparatus Used in Proving that Neutralization Is a Definite Act*

The experiment is most easily performed with the aid of burettes (Fig. 199), which are graduated tubes furnished with a stopcock at one end. The one is filled to the zero mark with the acid solution, the other with the basic. A measured volume of the one solution is drawn off into a small beaker, a few drops of an appropriate indicator added, and the second solution run in with constant stirring until the indicator just turns color. If the concentration of each solution is accurately known, it is easy to calculate, from the volumes required for neutralization, the ratio by weight between the acid and the base taking part in the action. Experiment shows that this ratio always bears a simple relation to that between the molecular weights of the reacting substances. The reaction

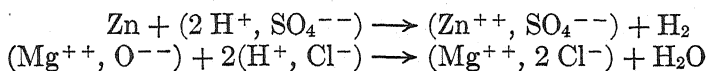
indicated in the equation $\text{NaOH} + \text{HCl} \rightarrow \text{NaCl} + \text{H}_2\text{O}$ (and similar ones) is perfectly definite, and knowing the weight of an acid employed, we can calculate the weight of the base required for its neutralization and also the weight of the salt formed.

Titration. In many other reactions besides those of neutralization, the quantities of reagents taking part in a reaction can be measured by using solutions of the reagents of known concentration, together

with some indicator that changes color when the reaction is just completed. This process is called *titration*, and the experimenter is said to *titrate* the one solution against the other.

Salts. It should be carefully noted that in a reaction of neutralization the removal of equivalent quantities of H^+ and OH^- ions through formation of neutral water leaves in solution equivalent quantities of the (positive) cations of the base and (negative) anions of the acid. If this solution is concentrated by evaporation, these ions build neutral crystals of solids called *salts*. *A salt, then, is, in general, a compound composed of equivalent metallic cations and acid anions.*

Salts may be formed in a number of reactions other than those of neutralization. For example, they are formed by the action of acids on metals or on oxides :

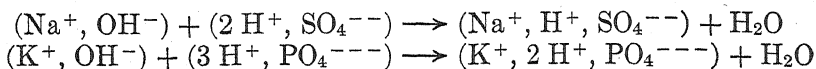


Varieties of salts. From this description one might expect each acid to form as many salts as there are hydroxides or metals. This is not true, however, because some of the expected salts are too unstable to be prepared. Still the number of salts is very large. Among all these salts it is convenient to recognize three general types.

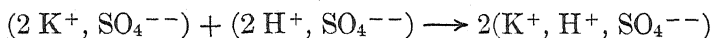
1. Normal salts. Salts such as those just described are called normal salts. *A normal salt is a compound built up wholly of the cations of any base and the anions of any acid.* In a molecular formula it may be thought of as derived from an acid by replacing all its hydrogen by an equivalent metal: thus $NaCl$, $ZnSO_4$.

General properties of normal salts. Since there is no one ion characteristic of normal salts, there are no properties which they all have in common. In solubility they range between wide limits, some dissolving to an extent of less than a milligram per liter, and others dissolving in much less than their own weight of water. In degree of ionization the salts are found to be much more nearly the same than is the case with either acids or bases. In a general way it may be said that *they are nearly all strongly ionized*. The color of a salt is due sometimes to the anion and sometimes to the cation out of which the salt is built. When both are colorless (as is true with the majority of both acids and bases), the salt is likely to be colorless. When either has a marked color, the salts are all apt to share it in some degree. Thus copper salts are usually some shade of blue or green, while the salts of the reddish chromic acid are usually yellow or orange.

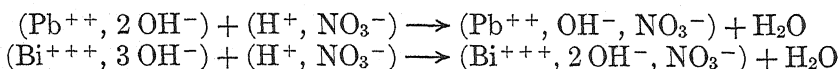
2. **Acid salts.** With solutions of acids having more than one replaceable hydrogen atom (polyhydric) we may add such a quantity of a base as is equivalent to only one equivalent (or two) of hydrogen. The other equivalents remain unchanged as ions:



The positive and negative ions remaining in solution then build crystals that may be represented by such formulas as KHSO_4 and KH_2PO_4 . In solution the crystals give again all three ions. Such salts are called acid salts. *An acid salt is a salt composed of both metallic and hydrogen cations, together with the anions of an acid.* It may be thought of as derived from an acid by the replacement of only a part of the available hydrogen by a metal. It is to be expected that in solution an acid salt gives the ions both of an acid and of a normal salt. Acid salts may also be formed in the way indicated in the equation



3. **Basic salts.** The reaction of a polyhydroxyl base with a monohydrogen acid in proper proportion leads to the formation of a *basic salt*:



A basic salt is a salt composed of metallic cations, together with both hydroxyl anions of a base and anions of an acid. It will be seen that in solution a basic salt gives the ions both of a base and of a normal salt.

Normal solutions and standard solutions. In scientific investigation, as well as in industrial analysis, it is often desirable to estimate the weight of acid or base in a given volume of solution by titration. For example, the pure-food laws of the Federal government, as well as the laws of the different states, require that all vinegars sold shall contain not less than 4 per cent of acetic acid; hence it becomes necessary to determine the percentage of acetic acid present in all such vinegars to see if they conform to the law. This may be readily accomplished by neutralizing a definite weight of the vinegar with a solution of a base the concentration of which is accurately known, as explained in connection with Fig. 199. Such a solution is called a *standard solution*. The standard may be of any

convenient concentration, depending upon the character of the solutions to be investigated. If the standard solution of an acid is prepared in such a way that 1 l contains 1 g-at. wt of replaceable hydrogen (1.008 g), then it is said to be a *normal solution*. Similarly, a normal solution of a base is one that contains 17.008 g (1.008 + 16) of the ion, OH^- , in 1 l. Solutions half this concentration are said to be half-normal ($N/2$). Tenth-normal solutions ($N/10$) are frequently employed.

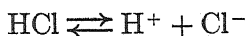
In order to prepare a normal solution of a monobasic acid such as hydrochloric acid, it is evident that one must have present in each liter of the solution 1 gram-molecular weight of the acid, since this amount would contain 1.008 g of hydrogen. Thus a normal solution of hydrochloric acid will contain 36.465 g of hydrogen chloride (1.008 g H + 35.457 g Cl). With dibasic acids, on the other hand, 1 l of the normal solution will contain only half the gram-molecular weight of the acid since each molecule contains two hydrogen atoms. The same general principles hold in the preparation of a normal alkaline solution, which contains 17.008 g of the OH^- ion per liter.

Such solutions greatly simplify calculations, for it is evident that 1 l of a normal solution of any acid will neutralize 1 molar weight of any mon-acid base; 10 cc will neutralize $\frac{1}{100}$ of its molar weight. If in neutralizing a solution of lye (NaOH) of unknown concentration 20 cc of normal acid is required, the solution of lye contains $\frac{20}{1000} \times 40.0048 (= 0.8000)$ g NaOH.

In a normal solution of a strong acid like hydrochloric there is present a greater concentration of hydrogen ions than there is in a normal solution of a *weak* acid like acetic. However, the concentration of potential hydrogen ions is the same in each solution. Consequently, the *same* amount of base is required to neutralize equal quantities of the two normal solutions. As rapidly as the hydrogen ions actually present in a solution of a weak acid enter into combination, other hydrogen ions are formed by the ionization of the weak acid.

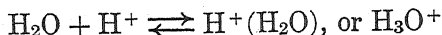
THE BRÖNSTED THEORY OF ACIDS AND BASES

The hydronium ion (H_3O^+). So far the hydrogen ion, formed by the ionization of an acid, has been indicated by the symbol H^+ :

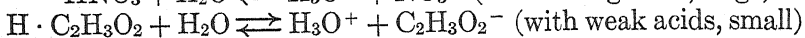


Now H^+ is a hydrogen atom that has lost its one valence electron and is the same as a proton, or nucleus, of a hydrogen atom. In volume it is much smaller than a hydrogen atom, and its electric

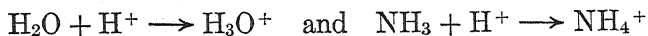
charge is very intense. It is not likely that it would wander at large in a solution, and there are many reasons for believing that it forms a rather loose attachment to a water molecule:



The resulting ion, H_3O^+ , is called the *hydronium* ion. The ionization of any acid is really a reaction with water:



The heat evolved in dissolving hydrogen chloride in water (p. 280) or in diluting a concentrated solution of a strong acid is in large part due to the reaction with water. As a rule, not much is gained by substituting the symbol H_3O^+ for that of the simple ion H^+ , and we shall do so merely in cases where it throws light on a reaction. For example, it is sometimes helpful to compare the two reactions

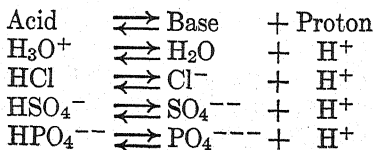


Acids and bases. There has always been a certain confusion in the use of the terms *acid* and *base*. For example, there has been much discussion of the question Which is the *acid*: the *compound* that is dissolved in water or the *solution* of the compound? Inasmuch as anhydrous hydrogen chloride, when liquefied, or dissolved in benzene, does not conduct electricity and has no action on metals, many argued that hydrogen chloride (covalent) is not an acid but that its aqueous solution (electrovalent) is. On the other hand, it has been demonstrated that a solution of hydrogen chloride in benzene, where there is no ionization, changes the color of indicators and exhibits certain catalytic effects in the same manner as aqueous solutions of acids. In a similar fashion, ammonia, NH_3 , shows basic properties under conditions in which there is no ammonium hydroxide (NH_4^+ , OH^-) present.

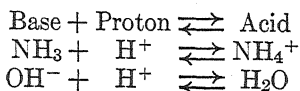
The Brönsted theory of acids and bases. This confusion in terms led the Dane Brönsted and others to a new point of view about acids and bases and a definition free from ambiguity. Brönsted defines an acid as *any substance which by its own ionization or in a reaction furnishes a proton*. The substance resulting from the loss of the proton is a base:



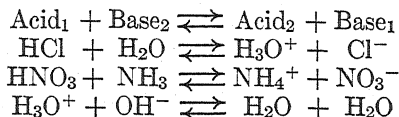
According to this definition, the term *acid* includes not only molecules, such as HCl , H_2SO_4 , and H_3PO_4 , but a great many ions, such as the following:



Similarly, bases include neutral molecules and a variety of ions of which hydroxyl is an outstanding example :



Actually no great concentration of free protons ever exists at any one time, and no acid surrenders its proton unless there is a base present to receive the proton. Hence all acid-base reactions involve two acids and two bases :



Such reactions involve proton transfer, just as oxidation-reduction reactions involve electron transfer. Neutralization thus appears as only one special type of acid-base reaction, but is of special significance because water is so frequently used as the medium for carrying out chemical reactions.

While the Brönsted theory is extremely useful in many connections, especially in the study of nonaqueous solutions, it does not in reality change the picture presented by the theory of ionization to any great extent. All acids in water yield protons (hydronium ions), and all bases hydroxyl ions ; so any measurement of the concentration of these ions is a true measure of the strength of an acid or a base.

Questions

1. Can you suggest any reason why sodium sulfate would not do as well as sodium chloride in the production of sodium by electrolysis?
2. In the Vorce cell, what properties must the porous diaphragm have to make it effective in preventing the action of chlorine on sodium hydroxide?
3. Hydrogen chloride contains hydrogen in addition to chlorine. Why, then, is a liter of chlorine heavier than a liter of hydrogen chloride?
4. Magnesium chloride (MgCl_2) and calcium chloride (CaCl_2) are both found abundantly in brines. Could chlorine be prepared from them by (a) electrolysis of the melted salts? (b) electrolysis of water solutions?
5. Citric acid is the acid that makes lemons sour, and has the composition represented by the formula $\text{C}_6\text{H}_8\text{O}_7$. It is a tribasic acid. (a) How would you modify the formula to express this fact? (b) What would be the formula of the calcium salt of this acid?
6. Are the hydroxides of *all* elements bases?

7. What is the difference between (a) an acid salt and a basic salt; (b) a normal salt and a normal solution?

8. Show how the three equations representing the reactions between sodium chloride, manganese dioxide, and sulfuric acid (p. 287) may be combined into a single equation.

Problems

1. Write the equations for the neutralization of (a) $\text{AgOH} + \text{H}_2\text{SO}_4$; (b) $\text{Ca}(\text{OH})_2 + \text{HNO}_3$; (c) $\text{Mg}(\text{OH})_2 + \text{H}_2\text{SO}_4$; (d) $\text{Al}(\text{OH})_3 + \text{H}_2\text{SO}_4$; (e) $\text{Ca}(\text{OH})_2 + \text{H}_3\text{PO}_4$.

2. A student wished to prepare chlorine by the action of hydrochloric acid on manganese dioxide. He used 50 cc of hydrochloric acid, density 1.2013. (a) What weight of manganese dioxide would be required to liberate the chlorine? (b) What volume of chlorine (standard) would result?

3. In normal times approximately 900 tons of chlorine are prepared daily in the United States by the electrolysis of sodium chloride. (a) What weight of sodium chloride is required daily in its preparation (assume that 5 per cent of the chlorine is lost)? (b) Calculate the weight of the sodium hydroxide formed. (c) Calculate the weight of hydrogen liberated in the process.

4. Calculate the weight (a) of sodium chloride and (b) of sulfuric acid required for preparing 100 kg of hydrochloric acid of density 1.1779.

5. What weight of sodium hydroxide will react with the hydrochloric acid obtainable from 10 kg of sodium chloride?

6. Calculate the weight of each of the following compounds required to prepare 1 l of the solution indicated: (a) normal solution of HCl ; (b) tenth-normal solution of H_2SO_4 ; (c) normal solution of $\text{H} \cdot \text{C}_2\text{H}_3\text{O}_2$ (acetic acid); (d) tenth-normal solution of NaOH .

7. Twenty-eight cubic centimeters of a normal solution of sodium hydroxide just neutralized 20 cc of a solution of sulfuric acid. Calculate the strength of the acid solution in terms of the weight of H_2SO_4 in 1 l of solution.

8. Forty cubic centimeters of a normal solution of sodium hydroxide was required to neutralize 12 cc of a solution of sulfuric acid. What volume of the latter is required to prepare 1 l of a normal solution of sulfuric acid?

Reading References

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- BRIGHTON. "Salt Making on the Great Salt Lake," *Journal of Chemical Education*, Vol. IX, pp. 407-415.
- DAVY. *The Decomposition of Fixed Alkalies and Alkaline Earths*, Alembic Club Reprints, No. 6.
- FOSTER. *Romance of Chemistry*. Chapter IX treats of acids, bases, and salts.
- GILBERT and others. "Sodium," *Industrial and Engineering Chemistry*, Vol. XXV, pp. 735-741.
- HOLMYARD. *Chemistry for Beginners*. Chapter VIII is entitled "Acids, Bases, and Salts." It is recommended to those who wish a simple, interesting discussion of these groups of compounds.
- HYLER. "The Production of Salt," *Journal of Chemical Education*, Vol. XII, pp. 203-207.
- KILPATRICK. "Acids, Bases, and Salts," *Journal of Chemical Education*, Vol. XII, pp. 109-111.
- STEINMAYER. "Salt Domes of Louisiana and Texas," *Chemical and Metallurgical Engineering*, Vol. XXXIX, pp. 388-389.
- THORPE. *Humphry Davy*. The fascinating story of the scientist who first isolated sodium and also proved that chlorine is an element.

The Chlorine Family

NAME	ATOMIC WEIGHT	MELTING POINT	BOILING POINT	COLOR AND STATE
Fluorine (F)	19.00	- 223°	- 187°	Pale-yellow gas
Chlorine (Cl)	35.457	- 101.6°	- 34.6°	Greenish-yellow gas
Bromine (Br)	79.916	- 7.2°	58.7°	Red liquid
Iodine (I)	126.92	113.5°	184.4°	Purplish-black solid

Characteristics of the family. The four elements in the table above form a strongly marked family and illustrate very clearly the way in which the members of a periodic family resemble each other. These four elements are often called the *halogens*, or "producers of salt." The distribution of the electrons in the atoms of each of the elements composing the family is shown in Fig. 200. The nuclear charge and completed shells of 8 and 18 electrons are designated, as well as the unoccupied positions in the valence (outer) shells.

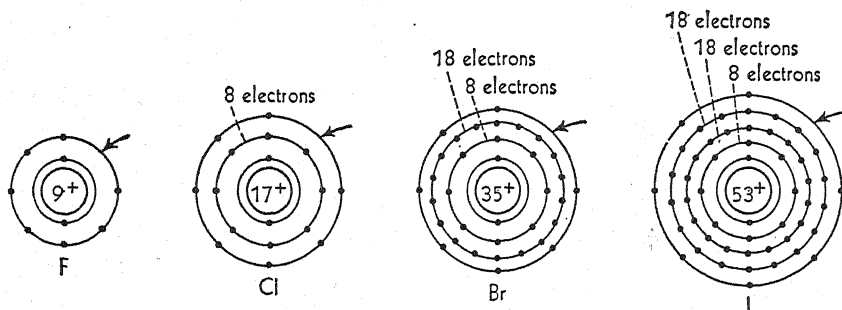


FIG. 200. *Electronic Diagrams of the Atoms of the Halogen Elements*

FLUORINE

History and occurrence. Fluorine occurs most abundantly in nature in the minerals fluorite, cryolite, and fluorapatite. *Fluorite*, or fluorspar, is calcium fluoride (CaF_2). It is found in many places, and in large deposits, especially in Illinois and Kentucky. *Cryolite*, a fluoride of sodium and aluminum (Na_3AlF_6), is found in Greenland and Iceland. *Fluorapatite* is the most abundant of the three and

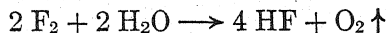
consists of calcium fluoride combined with calcium phosphate, as represented in the formula $\text{CaF}_2 \cdot 3 \text{Ca}_3(\text{PO}_4)_2$. Traces of compounds of fluorine are also found in sea water, in many minerals, in bones, and in the enamel of the teeth. In some localities compounds of fluorine occur in the drinking water. While the compounds of fluorine have long been known, all efforts to liberate the element failed until the year 1886, when the French chemist Moissan (Fig. 201) finally succeeded in isolating it and made an extended study of its properties and of its chemical activity toward other elements.



FIG. 201. Tablet Erected by the Associates and Friends of Moissan in His Laboratory in Paris, in 1906, on the Twentieth Anniversary of the Isolation of Fluorine

Method of preparation. Moissan electrolyzed a solution of potassium hydrogen fluoride (KHF_2) dissolved in liquefied hydrogen fluoride (HF). More recent experiments have shown that fluorine can be readily prepared, in large quantities if desired, by the electrolysis (in a copper cell) of a *melted* potassium hydrogen fluoride ($\text{KF} \cdot 3 \text{HF}$) with the use of pure graphite electrodes (Fig. 202).

Properties. Fluorine is a pale-yellow gas, 1.3 times as heavy as air. As with all other members of the family, its molecule is diatomic (F_2). It can be obtained as a yellow liquid which boils at -187° and solidifies at -223° . It combines with most of the metals and many of the nonmetals, sometimes so energetically as to produce light. Fluorine is probably the most active element known. It combines explosively with hydrogen, even in the dark and at low temperatures. It decomposes water, forming hydrogen fluoride and oxygen:



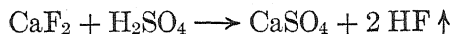
It was long believed that a part of the oxygen liberated in this reaction is converted into ozone, but more recent experiments show that the oxide F_2O is formed in this reaction. This oxide is very active, but less so than fluorine itself. Although the compounds of fluorine have many important uses, no uses for elementary fluorine have yet been developed.

Hydrogen fluoride. Vapor-density measurements indicate that the vapor of hydrogen fluoride is a mixture of molecules represented by the formulas HF and H_6F_6 , but it is customary to use the simpler formula, HF.

Pure hydrogen fluoride is best prepared by heating anhydrous potassium hydrogen fluoride in a platinum vessel:



It can also be prepared by the action of sulfuric acid on calcium fluoride:



This reaction is carried out in vessels of platinum or lead, and is the method commonly used in the preparation of the aqueous solutions of hydrogen fluoride, in which form hydrogen fluoride is ordinarily used.

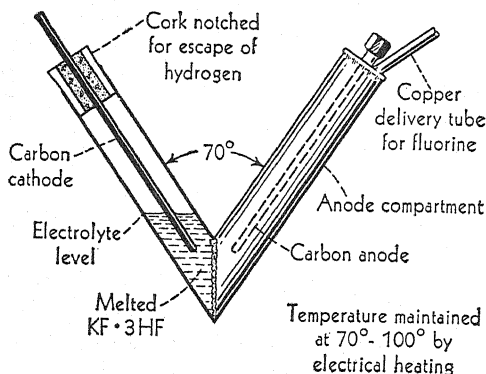
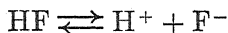


FIG. 202. Diagram of Apparatus for the Preparation of Fluorine

Properties. Hydrogen fluoride is a colorless liquid that boils at 19.4° . At low temperatures it forms a white solid melting at -83° . An aqueous solution containing 35 per cent of the compound has a constant boiling point at 120° under standard pressure, and distills with unchanged concentration.

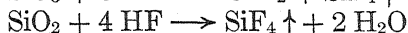
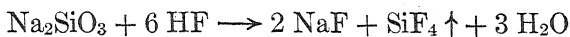
Hydrofluoric acid. Pure hydrogen fluoride is a nonconductor of electricity and is neutral in reaction. When dissolved in water it ionizes as follows:



The resulting solution is acid in character and is known as *hydrofluoric acid*. Ordinary commercial hydrofluoric acid contains about 50 per cent of hydrogen fluoride. Since this solution readily attacks glass, it is kept in bottles made of a wax called *ceresin*.

Hydrofluoric acid is a rather weak acid. It acts upon some of the metals, as well as upon their oxides and hydroxides, forming the corresponding salts. A single drop in contact with the skin produces a very painful wound, slow to heal. If inhaled, its vapor is very injurious.

A distinguishing property of hydrofluoric acid is its action upon glass. Ordinary glass consists principally of a mixture of sodium silicates and calcium silicates, together with an excess of silica (SiO_2). Hydrofluoric acid reacts with these silicates, forming solid fluorides of sodium and calcium, together with gaseous silicon tetrafluoride, SiF_4 . The equations for these reactions are as follows:



Advantage is taken of this property in marking thermometers and flasks, as well as in etching designs on glassware.

Etching glass. Etching with hydrofluoric acid is done in the following way: A piece of glass is covered with a thin coating of some wax, such as paraffin, by melting the wax on the glass and tilting the glass until it is completely covered with a thin film. After the wax hardens, the design is cut through it with a fine-pointed tool. The object so prepared is then exposed to the fumes of hydrofluoric acid. The acid attacks the glass wherever exposed, destroying its luster and leaving the design etched upon its surface.

Salts of hydrofluoric acid; the fluorides. The most important salt of hydrofluoric acid is the well-known mineral *fluorite* (CaF_2), or calcium fluoride. The fluorides of most of the metals can be prepared by the usual method for preparing salts, namely, by the action of the acid upon the metals directly or upon their oxides or hydroxides. A number of the univalent metals form acid salts, such as potassium hydrogen fluoride, KHF_2 .

CHLORINE

In the preceding chapter the preparation and properties of chlorine were described, together with those of hydrogen chloride and hydrochloric acid. At this point it may be added that chlorine is much less active than fluorine, and that hydrochloric acid is a much stronger acid than hydrofluoric acid.

BROMINE

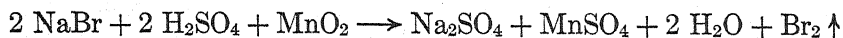
Occurrence. Bromine is one of the few elements that are liquid under ordinary conditions. It occurs in nature as the bromide ion in solutions of certain salts, principally those of sodium, potassium,

calcium, and magnesium. These salts are known as *bromides*. Bromides are present in sea water. Small percentages of bromides are found in the famous potash deposits at Stassfurt, Germany (see Stassfurt salts). They also occur in the waters of many springs and in the brine pumped from deep wells, especially in Michigan, mixed with much larger quantities of sodium chloride.

History. It was from salt brines that the German chemist Liebig first isolated bromine. He concluded, however, that the red liquid which he obtained was a compound of chlorine and iodine. A few months later (1826) the French chemist Ballard again obtained the substance from similar liquors. He rightly considered it to be an elementary substance, and, because of its disagreeable odor, named it *bromine*, from a word meaning "stench."

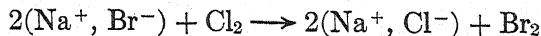
Preparation. The general methods used in the preparation of chlorine (p. 286) may likewise be employed in liberating bromine from its compounds.

Laboratory method. In the laboratory, bromine is prepared by the action of oxidizing agents upon hydrogen bromide. It is convenient to generate the hydrogen bromide in the course of the reaction by using a mixture of sodium bromide and sulfuric acid. The oxidizing agent ordinarily used is manganese dioxide. The reaction is exactly like that used in the preparation of chlorine (p. 286):



The bromide and manganese dioxide are thoroughly mixed and are then put in the retort *A* (Fig. 203), the end of which just touches the water in the flask *B*. The sulfuric acid is then added. When the retort is gently heated, the bromine is liberated, distills over, and collects under the water in the flask. The latter is kept cool by immersion in ice water in the beaker *C*.

Another method is based upon the fact that chlorine molecules will oxidize bromide ions (in solutions of bromides):



Extraction of bromine from the sea. Until recently the great center for the production of bromine in the United States has been in the vicinity of Midland, Michigan, where the bromine was recovered from natural brines pumped from deep wells. Smaller amounts were obtained from brines of the Ohio River valley and a

few other places. The Michigan brines contain about 25 per cent by weight of dissolved solids and about 1300 parts per million of bromine in the form of bromides. In 1924 about 2,000,000 lb of bromine was used in this country, and in 1931 about 9,000,000 lb. This sharp increase in demand resulted largely from the increasing use of bromine (as ethylene bromide, $C_2H_4Br_2$) along with tetraethyl lead in gasoline. It finally seemed desirable to call on the sea to yield up some of its enormous and inexhaustible supply of bromine.

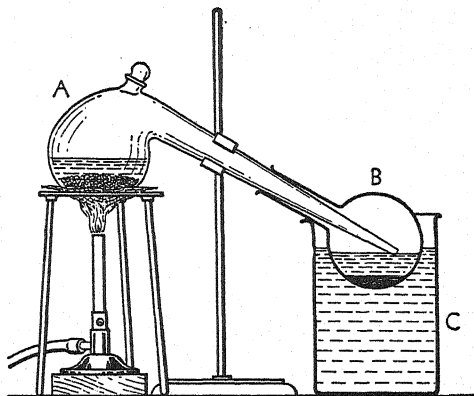
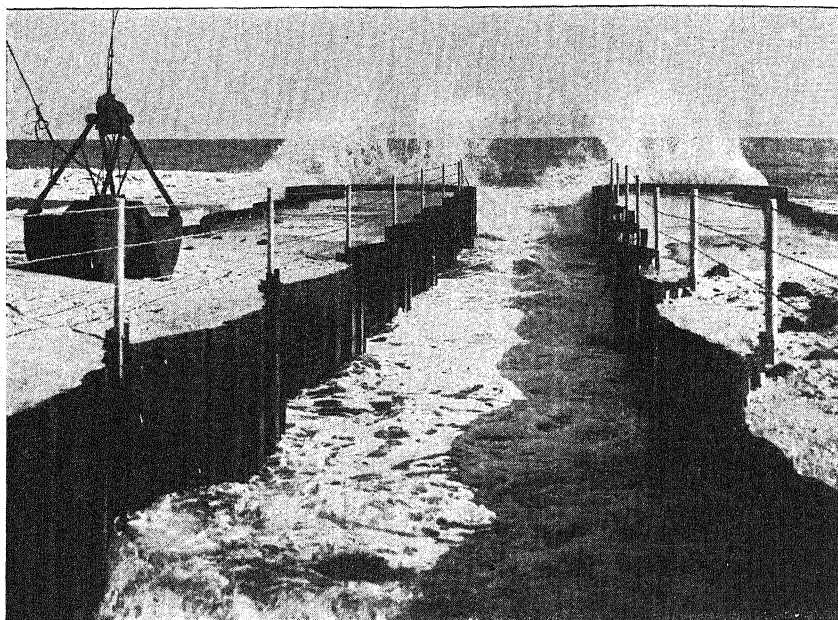


FIG. 203. *The Laboratory Preparation of Bromine*

Deep sea water carries only 67 parts per million of bromine (as bromides), but, even so, there are about 600,000,000 lb per cubic mile of water. In choosing a location for a recovery plant, it seemed necessary to find a site (on the beach) not too near the mouth of a river, so that the sea water would *not be diluted*; nor should the water be contaminated by organic matter. It was desirable to locate near a railroad; but railroad facilities are generally available near cities, and the coastal cities are invariably situated near the mouth of a river. All things considered, the small peninsula off Wilmington, North Carolina, separating the Atlantic Ocean from the Cape Fear River, seemed almost ideal for the purpose; and there the plant was built in 1934. From an intake (Fig. 204) which extends out into the surf, about 150,000 gal of raw sea water may be pumped per minute. First, it is pumped to a large pond, where an increase in the temperature of the water in warm weather brings an improvement in the efficiency of the extraction process during several months of the year. The water then goes to the extraction plant on the bank of the Cape Fear River; and after this water has been processed, the waste water is dumped into the river, which empties its own water into the ocean far south of the intake.

The actual recovery process first installed was a development of a method previously employed with the Michigan brines. The sea water, which is slightly alkaline, is first made slightly acid by the addition of about $\frac{1}{4}$ lb of sulfuric acid per ton of water. It is then sprayed into a

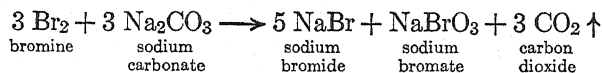


The Dow Chemical Company

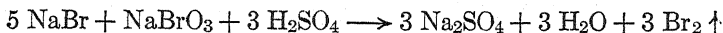
FIG. 204. *The Extraction of Bromine from Sea Water*

The picture shows the intake from which the sea water is pumped to a pond and then to the extraction plant

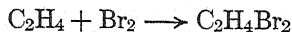
tower where it comes into contact with chlorine gas. The liberated bromine is blown out with air and is absorbed in a solution of soda ash (sodium carbonate, Na_2CO_3) :



The solution of the bromide and bromate is stored in tanks ; and when the bromine is needed, it is liberated by reaction with sulfuric acid :



The bromine is then allowed to react, in the presence of a catalyst, with ethylene gas, C_2H_4 , and ethylene dibromide is formed :



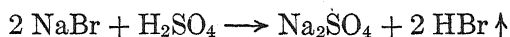
The efficiency of extraction of bromine from sea water by this process averages about 80 per cent, and the conversion to ethylene dibromide is about 90 per cent efficient. The plant has a daily capacity of more than 50,000 lb of bromine, and this can be increased if desired.

Properties. Bromine is a dark-red liquid whose density is 3.119. Its vapor has an offensive odor and is very irritating to the eyes and throat. The liquid boils at 58.7° and solidifies at -7.2° , but even at ordinary temperatures it has a high vapor pressure and forms a reddish-brown vapor. One hundred volumes of water dissolves about 1 volume of liquid bromine at 20° . The solution is called *bromine water*. Bromine is readily soluble in carbon disulfide and carbon tetrachloride.

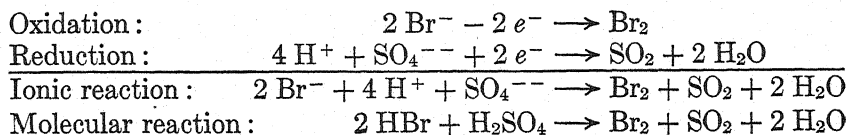
Chemical conduct. The chemical conduct of bromine is very similar to that of chlorine, except that it is less active. It combines directly with many of the same elements with which chlorine unites, but with less energy. Bromine water is often used as an oxidizing agent.

Uses. The demand for bromine has fluctuated greatly in recent years. Potassium and sodium bromides find use as medicinal agents, and silver bromide is used in photography. Today its chief use is in the preparation of ethylene bromide, a constituent of "ethyl gasoline." Bromine is also used in the manufacture of certain dyes and other organic compounds.

Hydrogen bromide. One would naturally expect that hydrogen bromide could be prepared in the same general way as hydrogen fluoride and hydrogen chloride, namely, by the action of sulfuric acid upon a bromide such as NaBr or KBr:

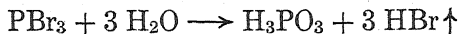


This reaction does indeed take place; the hydrogen bromide is evolved in the form of a colorless gas which fumes strongly in the air. At the same time *some bromine* is liberated, as is indicated by the formation of a reddish vapor. The odor of sulfur dioxide can also be detected. This method, therefore, cannot be used for the preparation of pure anhydrous hydrogen bromide, although it may be adapted to the preparation of a dilute aqueous solution. The reason why pure hydrogen bromide cannot be prepared by this method is that the bromide ion, unlike the chloride ion, is oxidized by the sulfuric acid:



Hydrogen bromide may be prepared by the direct action of bromine on hydrogen at moderate temperatures. However, the

method usually employed in the preparation of hydrogen bromide consists in the action of water upon phosphorus tribromide. The latter compound is a colorless liquid formed by the union of phosphorus and bromine, and has the formula PBr_3 . Water acts upon this compound with the formation of hydrogen bromide and phosphorous acid :



Experimental details. Some red phosphorus is put in a flask *A* (Fig. 205), and enough water is added to cover it. By means of the stopcock *E*, bromine is allowed to flow, drop by drop, from the funnel *B* into the flask. The phosphorus tribromide which forms in the flask then reacts with water. The U tube *C* contains glass beads which have been moistened with water and rubbed in red phosphorus. Any bromine escaping action in the flask acts upon the phosphorus in the U tube. The hydrogen bromide is collected in *D* by displacement of air. An aqueous solution of the gas is easily prepared.

Properties. Hydrogen bromide very strikingly resembles hydrogen chloride in its properties. It is a colorless, strongly fuming gas and may be condensed to a colorless liquid which boils at -67° .

It is very soluble in water. Under standard conditions 1 volume of water dissolves 612 volumes of the gas. The resulting solution has a density of 1.5 and contains 88 per cent of the gas. An aqueous solution containing 48 per cent of hydrogen bromide boils at 126° under ordinary pressure and distills with unchanged concentration.

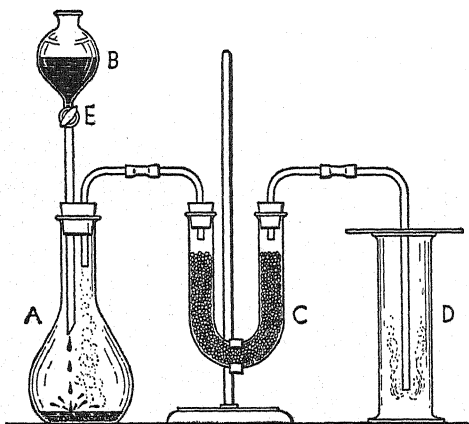


FIG. 205. *The Preparation of Hydrogen Bromide*

Chemical conduct of hydrobromic acid. Hydrogen bromide, like hydrogen chloride, has but little activity.

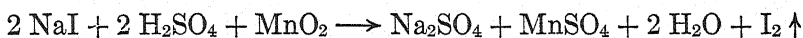
When dissolved in water it dissociates into the ions H^+ and Br^- , so that the solution is strongly acid and is known as *hydrobromic acid*. This acid is very similar to hydrochloric acid and reacts with metals and with their oxides and hydroxides, forming the corresponding bromides.

Salts of hydrobromic acid; the bromides. The bromides are, in general, very similar to the chlorides in their properties, and are prepared by the same general methods. The bromides of the common metals are all soluble except silver bromide, mercurous bromide, and lead bromide.

IODINE

History and occurrence. Iodine is present in sea water, but in such small percentages that it is difficult even to detect its presence. Certain seaweeds absorb the iodine from the water, and it was from ashes obtained by burning seaweeds (kelp) that the French chemist Courtois, in 1812, first isolated the element. Because of the violet color of its vapor he named it *iodine*, from a Greek word meaning "violet-colored." Iodine is also found in some marine animals, such as sponges, oysters, and some fishes. It occurs in the deposits of Chile saltpeter (sodium nitrate). It is interesting to note that the adult human body contains about 50 mg of iodine, approximately one third of which is in compounds in the thyroid gland; and it is generally believed that lack of iodine is the cause of certain forms of the rather common disease of this gland known as *goiter*.

Laboratory preparation. Iodine is set free from the iodides by the action of sulfuric acid and manganese dioxide. The reaction is similar to that which takes place in the liberation of chlorine from the chlorides and of bromine from the bromides.



Commercial production. Iodine is obtained on a very limited scale from the ashes of kelp (containing about 0.3 per cent of sodium iodide) burned on the shores of Scotland, Ireland, Japan, and France. The ashes are treated with chlorine or with manganese dioxide and sulfuric acid. The United States obtains about one sixth of its supply from the iodides in the California salt brines. In 1938 we produced 300,000 lb and imported 1,767,287 lb. The great world supply comes from the sodium nitrate beds of Chile, in which iodine occurs as sodium iodate (NaIO_3).

Purification of iodine. Iodine can be purified very conveniently by sublimation (p. 127) as follows: The crude iodine, mixed intimately with a little potassium iodide, is placed in a beaker *A* (Fig. 206), in the top of which rests a round-bottomed flask *B* containing cold water. The beaker is placed upon a sand bath *C* and gently heated. The iodine rapidly evaporates and condenses again on the cold surface of the flask in shining crystals.

Properties. Iodine is a purplish-black shining solid which, when sublimed, crystallizes in brilliant plates belonging to the rhombic system. It has a density of 4.93, melts at 113.5° , and boils at 184.3° . The element has a strong, unpleasant odor, although not so disagreeable as that of chlorine or bromine. Even at ordinary temperatures it gives off a beautiful violet vapor, which increases as heat is applied. It is only slightly soluble in water — 1 part in 3750 parts of water at 15° . It is very readily soluble in a solution of potassium iodide or of hydrogen iodide, forming a dark-brown liquid. It also dissolves in carbon disulfide, forming a violet-colored liquid.

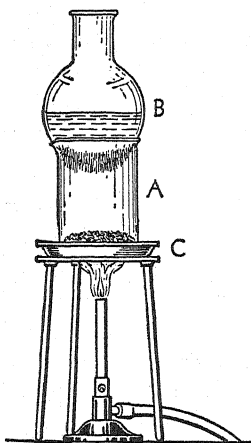
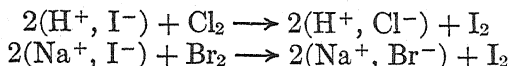


FIG. 206. *The Purification of Iodine*

Crystal lattice of iodine. Fig. 207 shows the crystal lattice of iodine. One of the interesting features about this lattice is that the iodine exists in the lattice as a twin atom, or dumbbell molecule. It will be recalled that measurements of gas density show many *gases* to be made up of diatomic molecules, such as H_2 , O_2 , N_2 , and Cl_2 . Here we have independent evidence, based on X-ray analysis, that iodine molecules are I_2 in the *solid* state.

Chemical conduct. Iodine is similar to chlorine and bromine in its chemical properties, but is less active. Both of the latter elements liberate iodine from its ions in solution (by oxidation) :



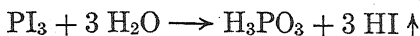
Like chlorine and bromine it combines directly with many of the metals, as well as with the nonmetals. In the presence of water it acts as a mild oxidizing agent.

A very characteristic property of iodine is its power of giving a blue color to a solution of starch. The reaction is carried out by adding a few drops of an aqueous solution of iodine to a test tube containing starch solution, and it is a very sensitive test either for free iodine or for starch.

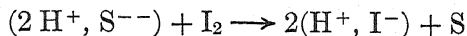
Uses. The chief use of iodine is in the manufacture of potassium and sodium iodides and of certain organic drugs and dyes. Silver iodide (AgI) is an important compound of iodine used in photography. The ordinary *tincture of iodine*, used largely as an antiseptic, is a solution of iodine and potassium iodide in alcohol; a colloidal

dispersion of the element is also used for the same purpose. Iodine is likewise a valuable reagent in the laboratory.

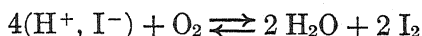
Preparation of hydrogen iodide. The method generally employed for the preparation of hydrogen iodide is similar to that used for the preparation of hydrogen bromide (p. 316) and consists in the reaction between phosphorus tri-iodide and water :



The hydrogen iodide is evolved as a heavy, colorless gas and may be collected by the displacement of air. Hydrogen iodide may also be obtained by passing a mixture of gaseous hydrogen and iodine vapor over a heated catalyst. An aqueous solution of the gas can be prepared by passing hydrogen sulfide into water containing finely divided iodine in suspension :



When the oxidation-reduction reaction is complete, the precipitated sulfur is removed by filtration. Solutions of the gas can be prepared in this way up to 50 per cent strength. The freshly prepared solution is colorless, but soon turns brown, owing to the liberation of iodine by the oxygen of the air :



It will be recalled that hydrogen bromide, because of its unstable character and the consequent ease with which it is oxidized, cannot be prepared in the pure state by the action of sulfuric acid on the bromides. Since hydrogen iodide is more unstable than hydrogen bromide, it is evident that this general method is still less adapted to its preparation.

Properties of hydrogen iodide. Hydrogen iodide resembles hydrogen chloride and hydrogen bromide in its physical properties, being a strongly fuming, colorless gas. It is easily condensed to a colorless liquid that boils at -35.5° under a pressure of 4 atm. At 10° about 450 volumes of the gas dissolves in 1 volume of water. A solution containing 57 per cent of hydrogen iodide boils at 127° and distills with unchanged concentration.

Chemical conduct. Owing to the ease with which the gas is decomposed into its elements, it acts in many respects like hydrogen, being a strong reducing agent. When dissolved in water it ionizes as follows :

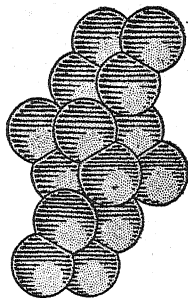
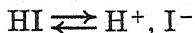


FIG. 207. *Crystal Lattice of Iodine*

This solution has strong acid properties due to the hydrogen ions present, and is known as *hydriodic acid*.

Salts of hydriodic acid; iodides. The iodides are similar to the corresponding chlorides and bromides but are not so stable toward heat. They are all solids and, with the exception of the iodides of silver, mercury, and lead, are soluble in water.

PERIODIC RELATIONS OF THE HALOGEN ELEMENTS

A review of the properties of the four halogen elements, and a comparison of their compounds, will show the relations that we expect among the members of a periodic family.

1. The first element (fluorine) stands somewhat apart from the others, while the latter have a close periodic relation. We shall find that this is a general rule in all families. Thus, oxygen stands apart from the other members in its family.

2. The physical constants of the elements vary somewhat regularly as we pass from element to element, as may be seen in the table at the head of this chapter.

3. The *type* of compound as shown in the formulas is much the same for all the elements, as is shown in the following table, though not all the elements form all the corresponding compounds:

HYDRIDES	OXIDES	OXYGEN ACIDS
HF	F_2O, F_2O_2	—
HCl	$Cl_2O, Cl_2O_6, Cl_2O_7, ClO_2$	$HClO, HClO_2, HClO_3, HClO_4$
HBr	Br_2O, Br_3O_8, BrO_2	$HBrO, HBrO_3$
HI	I_2O_4, I_4O_9, I_2O_5	$HIO, HIO_3, HIO_4, H_5IO_6$

4. The characteristics in any one series of compounds vary rather regularly as we pass from compound to compound, although fluorine is often an exception. This is shown in the following table:

Hydrogen fluoride (HF): a stable liquid boiling at 19.4° .

Hydrogen chloride (HCl): a stable gas liquefying at -85° .

Hydrogen bromide (HBr): an unstable gas liquefying at -67° .

Hydrogen iodide (HI): a more unstable gas liquefying at -35.5° .

THE OXYGEN COMPOUNDS OF THE HALOGEN ELEMENTS

Introduction. All the halogen elements form several oxides, and, with the possible exception of fluorine, they all form oxygen-containing acids and salts of such acids. Before taking them up as

individuals it is desirable to explain the system of naming the various acids and salts that has come into general use, not only for those of the halogens but for those of all the acid-forming elements.

Names of acids and their salts. Compounds of any kind that consist of but two elements are called *binary* compounds. Examples of binary *acids* are HCl, HI, H₂S. These acids are given names beginning with the prefix *hydro-* and ending in *-ic*; examples are hydrochloric acid, hydrosulfuric acid (H₂S). Salts of these acids have names ending in *-ide*; examples are sodium chloride, ferrous sulfide (FeS).

Compounds of any kind that consist of three elements are called *ternary* compounds. Most ternary *acids* contain oxygen and hydrogen in addition to an acid-forming element, and are called oxygen acids. The best-known acid of a given acid-forming element is given a name ending in *-ic*. Examples are nitric acid, sulfuric acid. The salts of such acids have names ending in *-ate*, as sodium sulfate, potassium phosphate (K₃PO₄). An acid with less oxygen than the *-ic* acid has a name ending in *-ous*, as nitrous acid (HNO₂), phosphorous acid (H₃PO₃); and the name of the derived salt ends in *-ite*, as sodium nitrite (NaNO₂), potassium phosphite (K₂HPO₃). If there should be an acid of still less oxygen content, its name begins with *hypo-* and ends in *-ite*, as hypophosphite. Sometimes there is an acid with still more oxygen than the best-known one, and the name then begins with *per-*, as perchloric acid. The salts of perchloric acid are perchlorates.

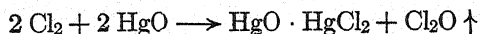
The acids of the halogen elements illustrate all these usages, and both acids and their salts may be tabulated as follows, the chlorine derivatives being used as an example:

ACID		SODIUM SALT	
Hydrochloric	HCl	Sodium chloride	NaCl
Hypochlorous	HClO	Sodium hypochlorite	NaClO
Chlorous	HClO ₂	Sodium chlorite	NaClO ₂
Chloric	HClO ₃	Sodium chlorate	NaClO ₃
Perchloric	HClO ₄	Sodium perchlorate	NaClO ₄

A salt having the formula NaHSO₄ is called sodium acid sulfate, sodium hydrogen sulfate, or, by an older name, sodium bisulfate.

The oxides of chlorine. The four known oxides of chlorine, namely, Cl₂O, Cl₂O₇, ClO₂, and Cl₂O₆, are all unstable, endothermic compounds. A brief discussion of three of these follows:

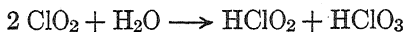
1. **Chlorine monoxide (hypochlorous anhydride) (Cl₂O).** This compound is prepared by passing chlorine through a tube containing mercuric oxide:



It is a highly explosive yellow gas, which condenses to a liquid at about 5°. With water it forms *hypochlorous acid*.

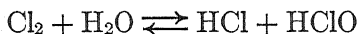
2. Chlorine heptoxide (perchloric anhydride) (Cl_2O_7). This oxide is a colorless oily liquid and explodes with great violence when brought into contact with easily oxidizable material or when struck. With water it forms *perchloric acid*.

3. Chlorine dioxide (ClO_2). Chlorine dioxide is a yellow gas which may be condensed to a liquid boiling at about 10°. It reacts with water to form a mixture of chlorous and chloric acids:



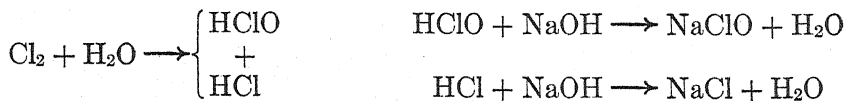
Hypochlorous acid and the hypochlorites. Both free hypochlorous acid and its salts (namely, the *hypochlorites*) are unstable. For this reason the acid has been obtained in dilute solution only.

1. Preparation. Hypochlorous acid forms as a product of an equilibrium reaction when chlorine is dissolved in water (p. 289):



This reaction is unusual in that it leads to the formation of *two* acids, one of which (HCl) is very strong and the other (HClO) very weak. If powdered calcium carbonate is suspended in the water into which chlorine is passed, the strong acid reacts with it as fast as formed and is removed as a factor in the equilibrium. This brings about a much larger production of hypochlorous acid (which does not decompose calcium carbonate). By distilling the resulting mixture a dilute solution of hypochlorous acid is obtained. A similar dilute solution can also be obtained by treating a salt of the acid with dilute sulfuric acid and distilling the product.

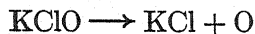
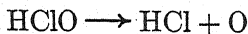
Dilute solutions of the hypochlorites of sodium, potassium, and calcium are formed, along with their chlorides, when chlorine is passed into *cold* solutions of their respective hydroxides. With sodium hydroxide the reactions proceed thus:



These equations, when combined, give the following:



2. Properties. Both hypochlorous acid and the hypochlorites are excellent oxidizing agents. In the presence of a substance that will combine with the oxygen formed, they decompose as follows:

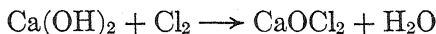


On the other hand, when their solutions *are heated*, hypochlorous acid and its salts change into the more stable form of chloric acid and chlorates respectively :



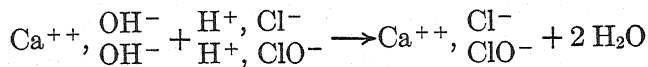
It is evident, therefore, that if one wishes to prepare hypochlorites, *the solutions must be kept cold.*

Bleaching powder (CaOCl_2). When chlorine is passed into a cold suspension of calcium hydroxide (ordinary slaked lime), there is formed a mixture of the chloride and hypochlorite of calcium, as explained above ; if passed over calcium hydroxide in the form of a dry powder, however, a white solid compound is formed known commercially as *bleaching powder*, or *chloride of lime* :

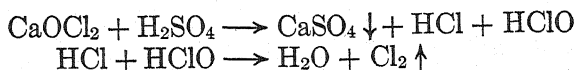


The reaction is never complete, however, so that the commercial product always contains some unchanged calcium hydroxide.

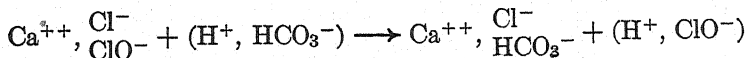
The constitution and reactions of bleaching powder. The constitution of bleaching powder is not known with certainty, but is generally regarded as represented by the formula $\text{Ca}^{++}, \overset{\text{Cl}^-}{\text{ClO}^-}$; in other words, it is a salt of both hydrochloric acid and hypochlorous acid. We may regard it as formed by replacing a hydrogen ion of each of these acids by an ion of bivalent calcium, thus :



Accordingly, if bleaching powder is treated with an acid of high boiling point, such as sulfuric acid (p. 367), we should expect both hydrochloric acid and hypochlorous acid to be evolved ; and this is what actually happens. If the solutions used are concentrated, then the two acids evolved react with each other to form free chlorine, and the reactions may be represented as follows :



If in place of sulfuric acid there is added a very weak acid, like carbonic, which ionizes to a very limited extent, *only hypochlorous acid is formed* :



This is the reaction that takes place when bleaching powder is exposed to air, the carbonic acid being formed from the carbon dioxide and moisture in the air. The hypochlorous acid is evolved slowly and is a good disinfectant.

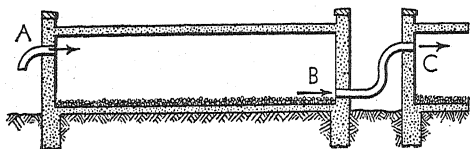
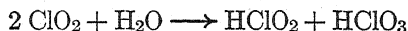


FIG. 208. *Preparation of Bleaching Powder*

Manufacture and uses of bleaching powder. Bleaching powder is made in large quantities by passing chlorine into large rooms at A (Fig. 208), over the floors of which is spread a layer of calcium hydroxide. The excess of chlorine leaves the room at B and enters a similar room at C. The resulting product is used commercially as a source of chlorine, since it is easily prepared and transported and the chlorine present can be liberated as desired. The commercial product usually contains from 35 to 37 per cent of available chlorine. It readily loses chlorine, however, especially at summer temperatures. It is stored and shipped in airtight packages or iron drums, to prevent decomposition from contact with air.

Uses of the hypochlorites. The hypochlorites, as well as the free acid, are excellent oxidizing and bleaching agents (p. 289). They also have a strong germicidal action. Many hypochlorite preparations are sold under various names by druggists, for use as disinfectants and antiseptics, and, if freshly prepared, are very efficient. Bleaching powder is used in large quantities for the same purposes, but liquid chlorine is displacing it to a large extent, as in the purification of water supplies and in bleaching.

Chlorous acid and the chlorites. Chlorous acid is formed in small quantities, along with chloric acid, when chlorine dioxide is dissolved in water:



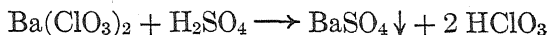
If this solution is neutralized with potassium hydroxide, a mixture of potassium chlorite and potassium chlorate results. Very recently methods have been developed for the industrial production of chlorites. They are coming into use as oxidizing agents in place of hypochlorites.

Chloric acid and the chlorates. The chlorates of the metals that form soluble hydroxides are prepared by passing chlorine into hot solutions of their respective hydroxides, as already explained (p. 323). With potassium hydroxide the reaction is expressed by the following equation:



When the resulting solution is evaporated, the potassium chlorate, being much less soluble than the potassium chloride, separates first, and by repeated crystallization can be obtained in the pure state.

From the chlorates, chloric acid itself can be prepared. The most convenient method consists in adding the calculated quantity of sulfuric acid to an aqueous solution of barium chlorate:



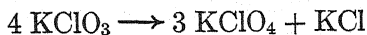
The insoluble barium sulfate separates as a white precipitate, which is removed by filtration, leaving a solution of chloric acid. This may be concentrated until it contains 40 per cent of acid. Further concentration leads to the decomposition of the acid, forming perchloric acid, water, and chlorine dioxide. The concentrated aqueous solution of the acid is a colorless liquid and has powerful oxidizing properties.

The chlorates can readily be obtained in the pure state, and are all soluble in water. Potassium chlorate and sodium chlorate are the most important of these salts.

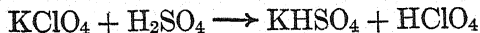
Commercial methods for preparing hypochlorites and chlorates. The method of preparing chlorates by passing chlorine into hot solutions of the hydroxide is a simple one but not economical. For example, in the case of potassium chlorate it will be seen by reference to the equation that only one sixth of the potassium in the hydroxide used is converted into the chlorate. Electrolytic methods are now used almost entirely for the preparation of both hypochlorites and chlorates.

It will be recalled that the electrolysis of a solution of potassium chloride or of sodium chloride results in the formation of chlorine, together with the corresponding hydroxide of the metal. It is possible so to regulate this process that the chlorine, instead of being evolved, is retained in the solution, together with the hydroxide, with which it interacts to form either the hypochlorite or chlorate.

Perchloric acid and the perchlorates. When potassium chlorate is heated, a portion of the compound changes into the perchlorate:



This reaction serves as a convenient method for preparing perchlorates, and perchloric acid itself can be obtained from these by the addition of sulfuric acid:



The perchloric acid formed is separated by distillation under diminished pressure (Fig. 209).

Pure perchloric acid is a colorless liquid. It is unstable, sometimes decomposing spontaneously with great violence. Like the

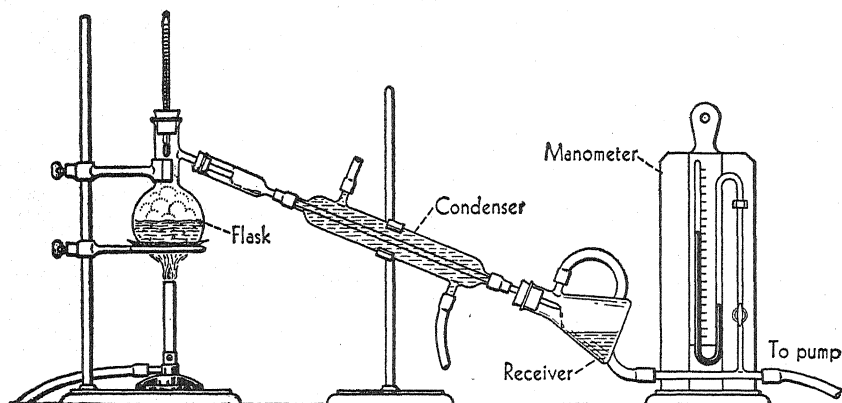


FIG. 209. *Distillation under Diminished Pressure*

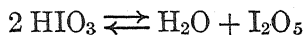
other oxygen acids of chlorine, it is an oxidizing agent. A concentrated solution of perchloric acid is now an article of commerce and finds a number of applications in analytical chemistry.

The perchlorates are readily prepared pure and are the most stable of all the salts of the oxygen acids of chlorine. When heated to high temperatures, they decompose into oxygen and the corresponding metal chlorides. Potassium perchlorate is one of the few compounds of potassium that are nearly insoluble in water (and still less soluble in alcohol), and advantage is taken of this property in an analytical procedure for determining the percentages of potassium present in different substances. Both chlorates and perchlorates are used as oxidizing agents, although the latter are gaining in favor because they are less hazardous.

Reactions taking place in the preparation of oxygen. It will be recalled that oxygen is commonly prepared in the laboratory by heating potassium chlorate. It is evident from the statements given above that two reactions take place concurrently when the potassium chlorate is heated: (1) the larger part is directly decomposed into potassium chloride and oxygen, and (2) the remainder is converted into potassium perchlorate and potassium chloride. The perchlorate, on further heating, is decomposed into the chloride and oxygen, so that all the oxygen in the potassium chlorate is ultimately evolved.

The oxygen acids of bromine and their salts. Three oxides of bromine are known, namely, Br_2O , Br_3O_8 , and BrO_2 ; and the following oxygen acids have been prepared in dilute solutions: hypobromous acid (HBrO) and bromic acid (HBrO_3). The hypobromites and bromates are very similar to the corresponding chlorine compounds and are prepared by the same general methods. From these salts the free acids can be prepared, as in the case of the corresponding chlorine compounds. The hypobromites are sometimes used as oxidizing agents, decomposing into oxygen and the corresponding bromide.

Iodine pentoxide (I_2O_5). Several oxides of iodine are known, of which the pentoxide is the most interesting. This is a white solid formed by heating iodic acid to 200° :



The reaction is reversible, for the oxide combines with water at ordinary temperatures to form iodic acid. At high temperatures it is decomposed into its constituent elements and acts as an oxidizing agent.

Iodic acid (HIO_3). This acid is formed by the action of sulfuric acid upon the iodates, although it is more convenient to prepare it by oxidizing iodine directly with nitric acid. It forms white crystals and is a strong oxidizing agent. A number of salts of iodic acid are known but are of relatively little importance. Sodium iodate (NaIO_3) is found in Chile saltpeter and is the principal source of iodine (p. 317).

Anhydrides of acids and of bases. In the last equation it will be noticed that the oxide I_2O_5 can combine with water to form iodic acid. Many nonmetallic oxides can combine with water in a similar way to form acids, and such oxides are called *anhydrides* of the acids, or *acid anhydrides*.

As we have seen (p. 185), many metallic oxides can combine with water to form bases, and such oxides are sometimes called *anhydrides of bases*, or *basic anhydrides*.

Questions

1. (a) What becomes of the calcium of glass when glass is etched by hydrofluoric acid? (b) Is the etched glass transparent or opaque?
2. For the equation on page 312, representing the preparation of bromine, write the oxidation and reduction (electron-transfer) equation.
3. None of the halogens occurs free in nature. Suggest a reason why this is so.

4. Iodine melts at 113.5° and boils at 184.4° . Why can it be purified by sublimation rather than by distillation?

5. What names would you give to the following acids and their salts: (a) H_2SO_4 ; (b) H_2SO_3 ; (c) H_2SO_2 ; (d) H_3PO_4 ; (e) H_3PO_3 ; (f) H_3PO_2 ?

6. What method of preparation is applicable alike to chlorine, bromine, and iodine?

7. How can you effect the following changes: (a) $\text{I}_2 \rightarrow \text{HI}$; (b) $\text{NaBr} \rightarrow \text{NaCl}$; (c) $\text{NaCl} \rightarrow \text{NaBr}$; (d) $\text{K}_2\text{SO}_4 \rightarrow \text{KI}$; (e) $\text{NaBr} \rightarrow \text{NaI}$?

8. Suppose you were given three bottles, each containing one of the following compounds: potassium iodide, sodium chloride, and potassium bromide, and were told to label each bottle properly. How would you proceed?

9. Why should sulfuric acid and carbonic acid act differently on bleaching powder?

Problems

1. If you had to prepare 100 g of silver iodide, (a) how would you proceed? (b) What weight of each of the compounds used would be required?

2. If you were given the problem of preparing 1 l of constant-boiling hydrobromic acid, (a) how would you proceed? (b) What weight of each of the compounds used would be required?

3. One liter of tincture of iodine contains 70 g of iodine and 50 g of potassium iodide dissolved in dilute alcohol. Suppose you had potassium iodide but no free iodine. (a) How would you proceed to prepare the tincture? (b) What weight of potassium iodide would be required?

4. Calculate the percentage composition of potassium iodate, KIO_3 .

5. On analysis a compound was found to have the composition 28.22 per cent K; 46.19 per cent O; 25.58 per cent Cl. (a) What formula do you calculate for the compound? (b) Is this the only possible formula?

Reading References

BEERY. *Stuff*. Chapter IV is entitled "The Wonders and the Horrors of the Halogens." Interesting, written in a popular style.

MANNING. "The Domestic Iodine Industry," *Chemical and Metallurgical Engineering*, Vol. XLI, pp. 568-570.

MIDGLEY and HENNE. "Organic Fluorides as Refrigerants," *Industrial and Engineering Chemistry*, Vol. XXII, pp. 542-545.

STEWART. "Commercial Extraction of Bromine from Sea Water," *Industrial and Engineering Chemistry*, Vol. XXVI, pp. 361-368.

WEEKS. "The Halogen Family," *Journal of Chemical Education*, Vol. IX, pp. 1915-1936. Tells the story of the discovery of each of the halogens.

YOST and HATCHER. "The Chemistry of Fluorine," *Journal of Chemical Education*, Vol. X, pp. 330-337.

Rate of Reaction and Equilibrium

RATE OF REACTION

Introduction. The main factors that influence the rate (or velocity, or speed) of a chemical reaction have already been briefly outlined in Chapter 6; and the general idea of equilibrium as a balance between two changes opposing each other has been suggested in a number of instances in the foregoing pages. It is now desirable to consider these important subjects somewhat more in detail.

Rate of a reaction. By the *rate* of a reaction is meant the mass of material undergoing transformation in a unit of time, such as a second, a minute, or an hour. In an entirely similar way we should say that the rate of mining coal is measured by tons mined per day. The mass transformed in a chemical reaction and the time can often be measured, with suitable experimental arrangements (Fig. 210).

It will help us in our understanding of the various factors controlling the rate of a reaction if we realize, in the beginning, that atoms, ions, and molecules do not react chemically with one another at a distance, but must come quite close together in collisions. It is generally only in this way that atoms can be gained or lost and that the switching of partners (an act common to many reactions) can occur.

Factors which influence the rate of a reaction. The important general factors which determine whether a reaction is to be fast or slow are (1) the nature of the reacting substances, (2) temperature, (3) catalysis, and (4) concentration. Let us now consider these separately.

1. **Nature of reacting substances.** The differences which we have often noted in the behavior of electrovalent and covalent substances

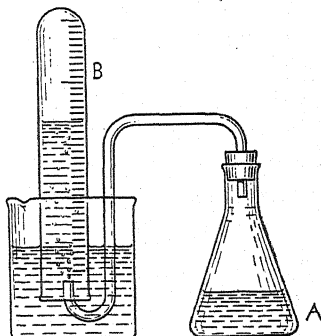
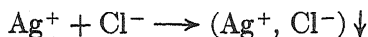


FIG. 210. *Measuring the Rate of a Reaction in Which an Insoluble Gas Is Generated*

The reaction is carried out in flask A, and the rate of reaction noted by the volume of gas collected in B in unit time

come again into evidence when rates of reaction are measured. The reactions between ions — for example,



generally occur almost instantaneously, and are so fast that it is extremely difficult to measure the rate. As fast as the ions are mixed together — in solution, for instance — so that they can collide, they tend to attract one another and combine. On the other hand, reactions involving *covalent molecules* generally proceed much more slowly, and often at a conveniently measurable rate. It is only this latter type of reaction which will be discussed in what immediately follows.

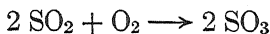
2. Temperature. A rise in temperature greatly increases the rate of a reaction. As a rough approximation it may be stated that a rise of 10° about doubles the rate. If, therefore, a reaction is proceeding at a given rate at 0° , it will go twice as fast at 10° and four times as fast at 20° . At 50° its speed will be 32 times as great as at 0° . Reactions whose speed is imperceptible at any ordinary temperature (for example, the oxidation of coal) may therefore become very rapid at a temperature within the reach of a Bunsen burner. On the other hand, we can greatly retard a reaction by keeping the material cold, as when we put food in cold storage.

Why does the reaction rate increase 100 per cent when the temperature is raised 10° ? The number of collisions between reactant molecules increases as the temperature rises, because of the greater velocity with which the molecules move (p. 74); but for a rise of 10° the increase in number of collisions is only a few per cent. The real explanation involves the well-known fact that molecules must not only collide, but collide with a characteristic *minimum violence* if their covalent bonds are to be broken and reaction is to take place. The molecules which react must be *activated*. A rise of 10° just about doubles the fraction of the molecules which possess enough energy to be activated, or "ripe," for reaction as collisions occur, and so the reaction rate is approximately doubled.

3. Catalysis. The increase of reaction rate in the presence of a suitable catalyst has already been mentioned in several instances (pp. 89, 172). A catalyst is generally supposed merely to modify the rate of a reaction which is already capable of taking place spontaneously without the catalyst. No energy is contributed by the catalyst to the reaction. In increasing the rate the catalyst may be said to function somewhat as a lubricant; but just how a catalyst performs its function is not very well understood.

Without doubt catalysts exert their influence in a variety of ways. Some appear to form, with one or more of the reacting substances, a definite but unstable compound which later undergoes decomposition or reaction of some sort and restores the catalyst which may then act over again.

Other catalysts seem to owe their efficiency to their very large surface, on which molecules of the reacting substances may become attached, or *adsorbed*, and thus be brought very intimately into contact. An excellent illustration of this effect is to be found in the manufacture of sulfuric acid by the *contact method*. Sulfur dioxide and oxygen react very slowly to form sulfur trioxide:



But in the presence of *metallic platinum*, upon the surface of which the molecules of both SO_2 and O_2 are adsorbed, the reaction proceeds with great rapidity.

Catalyst poisons. In the reaction we have just been considering, it is important that the sulfur dioxide gas and oxygen which are brought into contact on the platinum be very pure. Certain impurities, especially arsenic, even in extremely small traces, will cover up, or "poison," the platinum surface in such a way that there is no longer any available space upon which the molecules SO_2 and O_2 can "sit down."

4. Concentration. Since reactions take place between individual molecules, and since these cannot act upon each other at a distance, it will be seen that any condition which increases the frequency of molecular collision will promote the speed of reaction. The more reactant molecules there are crowded into a given volume, the faster will the reaction proceed. By "crowdedness" we mean *concentration* (p. 258). The greater the concentration, the better is the chance that molecules of one kind will find molecules of another kind with which they may react. It is a question of probability. It is probable that a hundred boys, all blindfolded and wandering about on a small dance floor in a perfectly random fashion, would collide with one another far more frequently than if they were moving about in the same way in the much larger space of a football field.

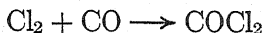
The law of mass action. As early as the beginning of the nineteenth century, Berthollet made important measurements on the effect of concentration, but it was not until 1867 that the dependence of the rate of reaction on concentration was definitely understood. In this year the Norwegian scientists Guldberg and Waage formulated and published the results of their investigations in the form

of the *law of mass action*, which states that the rate of a reaction is proportional to the active mass of each of the reacting substances. By "active mass" Guldberg and Waage meant what we define as *concentration*; and today the law might be very appropriately called the *law of concentration*.

The law of mass action holds true for a reaction, regardless of what units are used to express concentration — for example, regardless of whether concentration be expressed as grams per liter or as pounds per cubic foot. (The rate itself may be measured in various units, such as grams transformed per second or per minute; and the *numerical value* of the rate will depend on what units we choose.)

Concentration expressed as gram-molecular weights per liter. For the sake of convenience and especially for the sake of being able to keep track of the actual numbers of reactant molecules taking part in a reaction, we nearly always express concentration in terms of gram-molecular weights per liter (and the rate is measured as gram-molecular weights transformed, say, per second). We know, of course, that a gram-molecular weight of any substance contains the Avogadro number (6.06×10^{23}) of molecules. Usually the chemical reactions in which we are most interested take place in solution, although many common reactions occur between gas molecules. In both cases the concentration is expressed, as just indicated, as *molar* concentration (p. 258).

1. Illustration: a reaction between two molecules. To illustrate in a concrete way the principle of mass action we may consider the reaction between chlorine gas and carbon monoxide gas. They react to form the gas phosgene (COCl_2):



The rate of this reaction, according to the law of mass action, is proportional to the concentration both of the chlorine and of the carbon monoxide. Another way of saying the same thing is given in the equation

$$\text{Rate} = k \times [\text{Cl}_2] \times [\text{CO}]$$

where k is a constant and $[]$ is a symbol meaning "the molecular concentration of." In *actual magnitude* the rate will also depend upon the temperature, the presence of catalysts, and the properties of the reacting substances. At a given temperature and with a given chemical reaction, all these influences are constant in value; and we may designate their combined effect by the constant k , which is called the *rate constant*, or *velocity constant*, at that temperature.

Let us test the validity of the law of mass action experimentally by introducing into an evacuated glass vessel, of 1-liter volume, a known number of chlorine molecules, say 0.01 N , or $0.01 \times 6.06 \times 10^{23}$, namely a weight of $0.01 \times 70.914\text{ g}$; and at the same time introduce 0.01 N molecules of carbon monoxide ($0.01 \times 28\text{ g}$). By analysis of small samples, withdrawn from time to time from the reaction mixture, the rate of the reaction can be measured. The equation for the rate is

$$\text{Rate} = k \times 0.01 \times 0.01 \quad (1)$$

If, now, the concentration of chlorine, $[\text{Cl}_2]$, is doubled in the vessel, it is found by measurement that the rate is actually doubled:

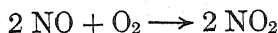
$$\text{Rate} = k \times 0.02 \times 0.01 \quad (2)$$

And if $[\text{CO}]$ is also doubled, the rate is four times what it was in (1):

$$\text{Rate} = k \times 0.02 \times 0.02 \quad (3)$$

Thus, once the reaction rate has been measured for any particular concentrations, the rate for any other concentrations can be predicted and verified. The temperature is kept constant throughout all these measurements.

2. Illustration: a reaction between three molecules. Let us carry through the same type of experiment with the gases oxygen and nitric oxide, which unite to form the brownish-colored gas nitrogen dioxide:



The rate and the rate constant k are found here to be quite different from what they are in the case of chlorine and carbon monoxide — and quite naturally so, because of the different nature of the reacting substances. Furthermore, since *two* molecules of nitric oxide react simultaneously with one molecule of oxygen, the mass action equation is to be stated thus:

$$\text{Rate} = k \times [\text{NO}] \times [\text{NO}] \times [\text{O}_2], \text{ or } k \times [\text{NO}]^2 \times [\text{O}_2]$$

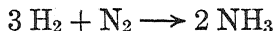
Let us test the validity of this equation by introducing the gases into the reaction vessel so that $[\text{O}_2] = 0.01$ and $[\text{NO}] = 0.02$, and measure the rate. Then keeping $[\text{O}_2] = 0.01$, if we double the concentration of nitric oxide, $[\text{NO}] = 0.04$, we find by actual test that the rate of the reaction is not doubled but quadrupled.

Similarly, for any reaction, the coefficients which show the number of the respective reactant molecules in the chemical equation are to be used as *exponents* for the respective concentrations in the mass-action equation.

Why are coefficients written as exponents? Again it is entirely a question of probability of collision. A very helpful analogy is afforded by the story of the blind giant who is catching and eating little boys locked up in a deserted house. If the giant has only one hand, the rate at which he can make his catches will be proportional to the crowdedness of the house with little boys. If the concentration is doubled, the rate is doubled. The giant can thus be likened to the CO molecule catching Cl₂ molecules at two different concentrations.

If, however, in a different setting, the giant has *two* hands with which he captures his victims, a doubling of the concentration of little boys will double the giant's rate of capture with each hand *at the same time*, or quadruple the rate at which the little boys disappear at the double concentration. Here we trace the resemblance to the oxygen-nitric oxide reaction.

When nitrogen and hydrogen react (p. 379), the nitrogen molecule plays the role of a three-handed giant,



and the mass action equation is

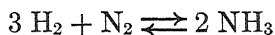
$$\text{Rate} = k \times [\text{H}_2]^3 \times [\text{N}_2]$$

Other factors affecting reaction rate. In addition to the four generally important factors which we have just been discussing, there are others which occasionally, in particular cases, exert a profound influence on the rate of a reaction. For instance, *radiant energy* will cause certain chemical changes to occur. In visible light photosynthesis (p. 157) takes place, and a photographic film is affected; ultraviolet light burns our skin; X rays and gamma rays decompose cancer cells. In all such photochemical reactions the rate depends on the intensity of the light. Then, too, certain inactive molecules may be *activated* by *bombardment* with alpha particles, electrons, or other fast-moving particles, or by the effects of a *silent electric discharge*, as in formation of ozone. The rate of a reaction may be greatly affected by the nature of the *solvent* in which the reaction is taking place. Also, the rate of reactions involving solids may depend on the *degree of subdivision* of the solids.

EQUILIBRIUM

Reversible reactions and equilibrium. We have seen that an equilibrium is "a balance between two changes opposing each other," and in a chemical equilibrium the opposing changes are the forward and backward parts of a reversible reaction.

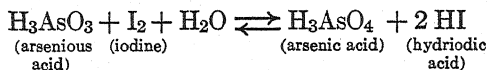
Experimental study shows that very many chemical reactions are reversible. The starting substances react with one another to form the products; and then the products, if they are not allowed to escape from the scene of action, react to give back the starting substances, at least to a certain extent. In the early stages the forward reaction attains its greatest rate, and then gradually becomes slower as the reactants are used up. On the other hand, the reverse reaction is relatively extremely slow in the beginning; but as the concentration of the products builds up, it becomes faster and faster. Eventually the reaction to the right (as it is written in a chemical equation) and the reaction to the left come to have the same rate, and are in balance. No further *net* transformation takes place. *This state of apparent rest is called equilibrium.* In reality both reactions continue, but at equal rates, and so the equilibrium is often called a *kinetic equilibrium*. An equation representing such a state of affairs, — for example



written with two reversed arrows, is called an *equilibrium equation*.

Equilibrium a kinetic state. While we have been quite sure that at equilibrium the two opposing reactions continue steadily at equal rates, until recently we have had no definite experimental method for proving that this is true. Neither the composition nor the concentration of anything taking part in the opposing reactions undergoes change when equilibrium has been established; so what can be measured to prove that the reactions are still going on? We should have to tag the atoms themselves in a compound on one side of the equation and see whether any of them presently turn up in compounds on the other side. Now this is just what has been done in recent years in the following way:

1. In solution arsenious acid is known to be slowly oxidized to arsenic acid by iodine, and an equilibrium is presently reached, as expressed in the equation



2. When equilibrium has been reached, the concentration of each of the participants in the reaction is carefully measured.

3. Arsenious acid is then prepared *that is radioactive*. This is done by bombarding arsenious acid (or the arsenic from which it is made) with neutrons (see cyclotron, pp. 247–248). This radioactive arsenious acid behaves exactly like ordinary arsenious acid in its chemical action.

4. A solution is now prepared in such a way that the concentrations of iodine, water, hydriodic acid, arsenic acid, and arsenious acid are exactly

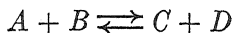
those found to be present at equilibrium in No. 2. However, *radioactive arsenious acid* is used instead of the ordinary acid.

5. If opposing reactions *stop* when equilibrium has been reached, the radioactive arsenious acid will be unchanged, and none of the arsenic acid will become radioactive.

6. After a time the arsenic acid is removed from the solution (by precipitation), tested with an electroscope (p. 221), and *found to be radioactive*, and to just the extent required by the calculated speed of the direct reaction.

This shows that *at equilibrium* the radioactive arsenious acid is being oxidized to give radioactive arsenic acid, and, since none of the concentrations change, the reverse reaction is also going on. In other words, an equilibrium is dynamic, not static.

Equilibrium constant. Let us set up a very general equation for a chemical reaction, in which the substances *A* and *B* react to form the products *C* and *D*:



At equilibrium the forward rate = the backward rate. But the forward rate = $k \times [A] \times [B]$, and the backward rate = $k' \times [C] \times [D]$. Therefore, since things equal to the same thing are equal to each other, it follows that

$$k \times [A] \times [B] = k' \times [C] \times [D]$$

This equation may be rearranged to the form

$$\frac{[C] \times [D]}{[A] \times [B]} = \frac{k}{k'} = K$$

where the ratio of the two velocity constants, k and k' , is equal to another constant, K , called the *equilibrium constant*. As is suggested by the name, the equilibrium constant is an *unchanging number* (at a given temperature) which is perfectly definite for any given reaction. If we can find a method for measuring the four concentrations in the equation *at equilibrium*, we can at once calculate the value of this constant. For example, let us suppose that at equilibrium and at 20° we can show that the following values of concentration *expressed in gram-molecules per liter* are found:

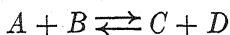
$$\begin{array}{ll} [A] = 0.6 & [C] = 0.4 \\ [B] = 0.6 & [D] = 0.4 \end{array}$$

When we substitute these values in the general equation, we have

$$\frac{[C] \times [D]}{[A] \times [B]} = \frac{0.4 \times 0.4}{0.6 \times 0.6} = K = 0.44$$

(In equilibrium-constant equations of this kind it is customary to indicate the products of the reaction in the numerator and the reacting substances in the denominator.)

Effect of changes in concentration on equilibrium. If we bring together these four substances in some proportion other than that required by the constant K , the reaction will go on in one or the other direction until the four concentrations attain values that once more give $K = 0.44$. If we greatly increase the concentration of some one of the components (say B), then all the other concentrations must change. It will be seen that in this case the concentration of A must become less, and that of both C and D greater, to bring the ratio of numerator and denominator back to the original value of $K = 0.44$. In other words, we cause the equilibrium expressed in the equation



to shift toward the right. We often add a large excess of one component in this way to push the reaction as near to completion as possible.

Equilibrium constant for some familiar reactions. Let us write the expression for the equilibrium constant for a few of the reactions referred to in the preceding pages of this book; and as we do so, let us remember that *coefficients* are to appear as *exponents* of concentration.

For $2 \text{H}_2 + \text{O}_2 \rightleftharpoons 2 \text{H}_2\text{O}$, we have $\frac{[\text{H}_2\text{O}]^2}{[\text{H}_2]^2 \times [\text{O}_2]} = K$

For $3 \text{O}_2 \rightleftharpoons 2 \text{O}_3$, we have $\frac{[\text{O}_3]^2}{[\text{O}_2]^3} = K$

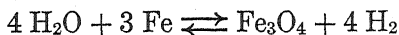
And for $\text{H}_3\text{AsO}_3 + \text{I}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{AsO}_4 + 2 \text{HI}$, we have

$$\frac{[\text{H}_3\text{AsO}_4] \times [\text{HI}]^2}{[\text{H}_3\text{AsO}_3] \times [\text{I}_2] \times [\text{H}_2\text{O}]} = K$$

To get the numerical values of K in these various equilibria we must, of course, know the concentrations of reactants and products at equilibrium.

Active mass of a solid. A reaction taking place in a mixture of gases or in solution is said to be *homogeneous* because the concentration of each component is the same in every part of the mixture. This concentration can be stated in gram-molecules per liter. When a *solid* is acted upon by a gas, as in the reaction of steam upon iron, or by a liquid, as when hydrochloric acid acts upon zinc, the reaction is said to be *heterogeneous* because some of the components present

do not mix with one another. When steam and hot iron react in a closed vessel, an equilibrium is established according to the equation



We have no difficulty in defining the concentration of the steam and in seeing that every molecule of it is available for the reaction. With the iron the case is different. Only those atoms forming the surface of the solid, or given off as vapor, can have any effect upon the velocity of the reaction at a given time; and in either case the effect will be practically constant. *That portion of a substance which is available for a reaction at a given time is called its active mass*, and it is with the active mass that the law of mass action is concerned. The best we can do in regard to the active mass of a solid is to consider it as a constant during the reaction. If, in the equilibrium equation

$$\frac{[\text{H}_2]^4 \times [\text{Fe}_3\text{O}_4]}{[\text{H}_2\text{O}]^4 \times [\text{Fe}]^3} = K'$$

we consider $[\text{Fe}_3\text{O}_4]$ and $[\text{Fe}]$ as constants and incorporate them in K' , we get

$$\frac{[\text{H}_2]^4}{[\text{H}_2\text{O}]^4} = K$$

as the equilibrium constant for this reaction.

Reactions of dissociation. There is a type of chemical reaction, many examples of which are known, in which a solid decomposes, or *dissociates*, into a second solid and a gas. Thus the carbonates when heated yield an oxide of the metal and carbon dioxide:



We express the equilibrium constant for this reaction thus:

$$\frac{[\text{CaO}] \times [\text{CO}_2]}{[\text{CaCO}_3]} = K'$$

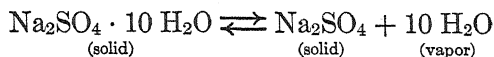
But both CaO and CaCO_3 are *solids*, and their active masses or concentrations may each be regarded as constant and may be designated by k' and k'' . We shall then have

$$\frac{k' \times [\text{CO}_2]}{k'} = K', \quad \text{or} \quad [\text{CO}_2] = \frac{K' \times k''}{k'} = K$$

In other words, the concentration of CO_2 in equilibrium with CaO and CaCO_3 must be *constant* at a given temperature. But the concentration of a gas is proportional to its pressure; so we may say

that at a given temperature the *pressure* of CO_2 in contact with CaO and CaCO_3 is *constant*. This constant pressure, due to the gas formed, is called the *dissociation pressure* of the solid from which the gas is formed.

Efflorescence of hydrates. An entirely similar case is presented by many hydrated salts which tend to lose water (as vapor) and form a lower hydrate or an anhydrous salt, thus:



At a definite temperature the salt will give off water vapor until equilibrium is reached with the two solids concerned in the reaction. In the open air, where the water vapor can continually escape, no equilibrium can be reached, *unless the partial pressure of the water vapor present in the air is equal to the dissociation pressure of the hydrate*. If this partial pressure is *equal to* (or greater than) the dissociation pressure of the hydrate, no dissociation occurs. If it is *less*, the hydrate steadily loses water vapor to the air, and usually crumbles to powder consisting of the anhydrous salt or a lower hydrate. Loss of water in this way is called *efflorescence*, and the hydrate is said to be *efflorescent* in air.

The principle of Le Chatelier. An equilibrium, once established, tends to maintain itself indefinitely if it is not disturbed from the outside. We have already seen that an equilibrium may be shifted by the addition of an excess of a reagent (p. 337); and, in general, an equilibrium may be shifted by various kinds of forces, stresses, or changes in environment which are brought to bear on the equilibrium. There is a far-reaching generalization, called the principle of Le Chatelier, which deals with changes in an equilibrium of any sort, either chemical or physical. Le Chatelier's principle may be stated as follows: *If a stress is brought to bear upon an equilibrium, the equilibrium will shift in such a way as to diminish the stress so applied*. This principle is extremely helpful to us in our thinking because it allows us to predict what will happen to an equilibrium when it is disturbed.

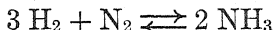
Illustrations of Le Chatelier's principle. To show how the predictions are made, a few illustrations are given.

1. An added excess of reactant will cause an equilibrium to shift toward the *product* side because in this way the excess (or some of it) will be used up. An added excess of product will drive the equilibrium the other way.

2. If ice, in equilibrium with water, is subjected to a definite

pressure, it will melt because a given weight of water occupies less volume as a liquid than as a solid. As the ice melts, the pressure is relieved.

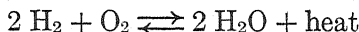
3. Similarly the application of pressure to a mixture of hydrogen, nitrogen, and ammonia gases in equilibrium,



will shift the equilibrium toward the right, since nitrogen and hydrogen combined as ammonia occupy only half as much volume as when free.

4. Substances which dissolve with the absorption of heat (as most substances do) will become more soluble as the temperature is raised. More of the substance will dissolve to absorb the applied heat.

5. All chemical reactions involve changes in energy, and in a chemical equilibrium one reaction evolves energy while the reverse reaction absorbs energy. To increase the temperature favors the heat-absorbing reaction. For example, the equilibrium



shifts toward the left if the temperature is increased.

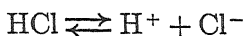
Illustration of combined effects. In Chapter 20 we shall see that the manufacture of sulfuric acid depends upon the reaction expressed in the equilibrium equation



The industrial problem is to push the yield as far as possible toward the production of SO_3 , and at a low cost. It will be necessary to take into account the following considerations: (1) The law of mass action suggests that we increase the O_2 much beyond the quantity required by the equation because the oxygen is furnished by the air and is cheap. (2) There is a decrease in volume in the reaction; so we should apply pressure to the system if this is at all economical. (3) Heat is evolved, and if the reaction goes at all fast, the rise in temperature will diminish the yield because the reverse reaction will be stimulated. Therefore we should cool the reaction mixture by suitable methods. (4) But cooling will slow up the reaction with a loss of time. Therefore we should seek a catalyst that will speed up the reaction at a lower temperature.

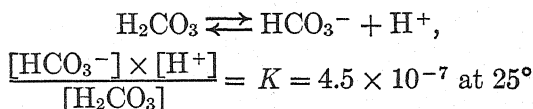
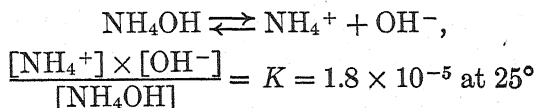
Equilibrium and electrolytes. The reaction rates of electrovalent compounds (electrolytes) are so fast that we have difficulty in measuring them. Yet such reactions are reversible, generally with both forward and backward reactions fast; and we may have true chemi-

cal equilibria involving ions in solution. These equilibria are represented in the usual way — for example,



But it has been found that the equilibrium constant K for strong electrolytes (all salts and many acids and bases) is *not* constant. Probably the attractions and repulsions of the charged ions interfere with mass action. By using so-called "activities" instead of *concentrations* good equilibrium constants can be obtained; but a discussion of this method is beyond the scope of this book.

On the other hand, *weak* electrolytes obey the law of mass action fairly well, and reasonably steady values for the equilibrium constants may be calculated for the ionization equilibrium of such weak acids and bases as ammonium hydroxide and carbonic acid:



Such constants are of great utility in the treatment of equilibria of weak electrolytes.

Ion equilibrium for water. Water ionizes slightly according to the equation $\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$. Exact measurements have shown that at ordinary temperature $[\text{H}^+] = 1 \times 10^{-7}$ and $[\text{OH}^-] = 1 \times 10^{-7}$, or the concentration of each of these ions is 0.0000001 *N*. Because of the relatively great mass of water, $[\text{H}_2\text{O}]$ is practically constant, and we may simplify the equation for the equilibrium constant as follows:

$$\frac{[\text{H}^+] \times [\text{OH}^-]}{[\text{H}_2\text{O}]} = K', \text{ or } [\text{H}^+] \times [\text{OH}^-] = [\text{H}_2\text{O}] K' = K = 1 \times 10^{-14}$$

If we add an acid to the neutral water, $[\text{H}^+]$ goes up and $[\text{OH}^-]$ goes down; if we add a base, $[\text{OH}^-]$ is increased and $[\text{H}^+]$ must diminish. But their product, $[\text{H}^+] \times [\text{OH}^-]$, still keeps the constant value 10^{-14} , regardless of other ions added to the water.

pH value. Very slight changes in acidity and alkalinity are frequently of great significance, and the values of small concentrations of hydrogen or hydroxyl ions have to be written and referred to very often. It has become customary to indicate these by merely stating

the value of the *exponent* of the normal concentration (omitting the minus sign). This value of the hydrogen ion concentration is designated by the symbol *pH*. Thus we say that the *pH* value for water is 7, meaning that in 1 l of water the concentration of the H^+ ion (and also that of the OH^- ion) is $1 \times 10^{-7} N$. Using this method of representation we may construct the following table :

CONCENTRATION OF H^+ <i>N</i>		<i>pH</i>	CONCENTRATION OF OH^- <i>N</i>
1	10^0	0	10^{-14}
0.1	10^{-1}	1	10^{-13}
0.01	10^{-2}	2	10^{-12}
0.0001	10^{-4}	4	10^{-10}
0.0000001	10^{-7}	7	10^{-7} (neutral water)
0.0000000001	10^{-10}	10	10^{-4}
Etc.	Etc.	Etc.	Etc.

Thus, as the acidity *decreases*, the *pH* value (by definition) *increases*. A solution of *pH* value greater than 7 is *alkaline*.

The ordinary blood of a healthy human being is slightly alkaline, with a *pH* value of about 7.2; that is, the H^+ concentration is between 10^{-7} and 10^{-8} . More OH^- ions are present than H^+ ions. After a heavy meal the *pH* value of the blood increases a little more, which means that the blood becomes still more alkaline. This is no doubt a result of the withdrawal of effective H^+ ions from the blood by the stomach to form hydrochloric acid, which is employed in the digestion of the food.

THE THEORY OF PRECIPITATION

Solubility product. If a saturated solution of barium sulfate is prepared by dissolving pure barium sulfate in pure water at room temperature, the concentration of the solution is very small; that is to say, barium sulfate is but very slightly soluble. *Actual measurement* shows that at 18° only 2.3 mg of barium sulfate is contained in 1 l of the saturated solution. This amounts to 0.00001 g-mol./l.

Now, since barium sulfate is a typical salt, it is completely ionized in such a dilute solution. Consequently the concentration of the barium ion $[Ba^{++}]$ will be 0.00001 gram-ion per liter (g-ion/l), and that of the sulfate ion $[SO_4^{--}]$ will also be 0.00001 g-ion/l. *The product of the concentration of the two ions of a salt in a saturated solution is called the solubility product of the salt.*

$$[Ba^{++}] \times [SO_4^{--}] = K_{s.p.} \text{ (solubility product)}$$

For barium sulfate $K_{s.p.}$ would have the value 0.00001×0.00001 , or 1×10^{-10} .

The conditions of precipitation. It has been found *experimentally* that whenever the product of the concentrations of the barium ion [Ba^{++}] and the sulfate ion [SO_4^{--}] exceeds the solubility product of barium sulfate, the two ions begin to build up crystal lattices of barium sulfate and leave the solution as a precipitate until the solubility product is again reached. It makes no difference what the source of the two ions may be. For example, the two ions may be supplied by adding barium chloride and sulfuric acid to the water, and they need not be added in equivalent amounts; that is, the concentration of the two need not be the same. As long as the product of the two concentrations (expressed in gram-ions per liter) exceeds $K_{s.p.}$, precipitation results and continues until the product of the two ion concentrations comes down to this value. Since every substance has at least *some* solubility, precipitation will never be complete.

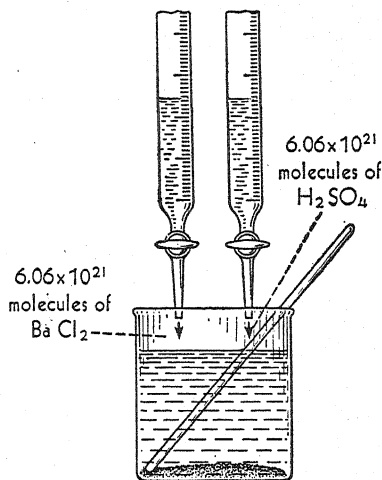
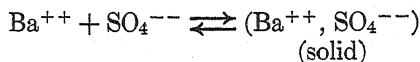


FIG. 211. *Precipitation of Barium Sulfate*

The principle of solubility product applies quite generally to all types of precipitation, and is of great service in the study of the formation of insoluble compounds from solutions.

Solubility product and the mass law. It is possible to deduce the law of the constancy of the solubility product from the mass law as applied to the equilibrium of ions (p. 337); but such a demonstration is beyond the scope of the present text. The significant thing is that *experimentally* the law of solubility product is found to be true.

Common-ion effect. Suppose that barium chloride and sulfuric acid are allowed to react in exactly equivalent amounts, say 0.01 g-mol. wt of each (Fig. 211):



Then, after the precipitate has settled, a still further slight precipitation from the saturated solution can be obtained by adding an excess of *either* Ba^{++} *or* SO_4^{--} . This we might well expect, not only from the solubility-product law, but also from Le Chatelier's principle. Such a displacement of an ion equilibrium by addition of a common ion is called the *common-ion effect*. It has many applications in driving or forcing ion reactions almost entirely to completion.

Applications of the law of solubility product. With the law of solubility product in mind we find that three general cases for its application present themselves for study.

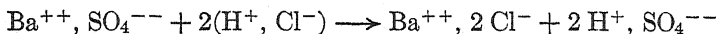
1. *Double decomposition between two salts.* When two salts, such as CuSO_4 and BaCl_2 , are brought together in solution, we have an abundance of all four ions Cu^{++} , SO_4^{--} , Ba^{++} , and Cl^- . When any pair of these ions exceed their solubility product, they begin to grow into crystal lattices and precipitate. Of these four possible combinations the solubility product of BaSO_4 is by far the smallest. Consequently barium and sulfate ions will leave the solution as a crystalline precipitate of barium sulfate until the remaining concentrations of these two ions satisfy the equation

$$[\text{Ba}^{++}] \times [\text{SO}_4^{--}] = K_{s.p.}$$

2. *Double decomposition between a salt and a strong acid.* If we bring together a salt and a *strong acid* (for example, BaCl_2 and H_2SO_4), the conditions of equilibrium are practically the same as in the case of two salts; for both compounds are freely ionized, and all the ions are free to set up new equilibria. Precipitation of BaSO_4 will occur until the concentrations of the Ba^{++} ion and the SO_4^{--} ion are diminished to satisfy the solubility product

$$[\text{Ba}^{++}] \times [\text{SO}_4^{--}] = K_{s.p.}$$

On the other hand, the insoluble precipitate *will not dissolve in even a strong acid*, such as HCl ; for if it were to dissolve according to the equation



the concentration of Ba^{++} and SO_4^{--} would almost at once reach values such that

$$[\text{Ba}^{++}] \times [\text{SO}_4^{--}] > K_{s.p.}$$

and precipitation would occur. *The insoluble salt of a strong acid is insoluble in acids as well as in water.*

3. *Double decomposition between a salt and a weak acid.* If we bring together a salt and a *weak acid*, the conditions are notably different from those of the two former cases. The salt is freely ionized, *but the acid will supply few active ions*. For example, BaCO_3 has about the same solubility as has BaSO_4 , and the solubility product is therefore about the same for the two salts.

$$[\text{Ba}^{++}] \times [\text{CO}_3^{--}] = K_{s.p.} \text{ (a very small constant)}$$

When we bring together BaCl_2 and H_2CO_3 , however, we obtain no precipitate, for the reason that H_2CO_3 furnishes very few active CO_3^{--} ions; and although the concentration of the barium ions $[\text{Ba}^{++}]$ may be rather large, the concentration of the carbonate ions $[\text{CO}_3^{--}]$ is so small that the *product* of the two never exceeds the solubility product $K_{s.p.}$

The reaction does go on to a slight extent, forming BaCO_3 in solution, according to the equation



But the HCl produced is *freely ionized*, and the H^+ ions from this source at once diminish still further the small ionization of H_2CO_3 , as may be seen from the equilibrium equation

$$\frac{[H^+] \times [H^+] \times [CO_3^{--}]}{[H_2CO_3]} = K \text{ (very small)}$$

Any H^+ added from another source (as from H^+ , Cl^-) will increase the H^+ in the numerator of the equation, causing H^+ to combine with CO_3^{--} to restore equilibrium and so diminish the concentration of CO_3^{--} .

On the other hand, if we expose the insoluble $BaCO_3$ to the action of a strong acid (such as H^+ , Cl^-), it will dissolve; for, as fast as the salt forms a saturated solution according to the solubility equation

$$[Ba^{++}] \times [CO_3^{--}] = K_{s.p.}$$

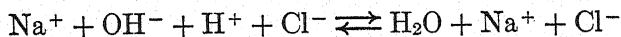
the H^+ ions of the added acid at once combine with the CO_3^{--} ions supplied by the solubility equilibrium to form *nonionized* H_2CO_3 . More $BaCO_3$ then passes into solution, and the process continues until all the salt has dissolved. *The insoluble salt of a weak acid will dissolve in a strong acid.*

Precipitation in case of extremely insoluble compounds. From the explanation that has just been given, it will be seen that if a given salt has an *extremely small solubility*, then even a weak acid may precipitate it. For example, most of the sulfides of the metals are "insoluble" in water; but some are very much more insoluble than others. Consequently the weak acid H_2S will precipitate the most insoluble ones even in the presence of a strong acid, but it is too little ionized to precipitate the more soluble ones even in neutral solution. Many of the reactions employed in analytical chemistry depend on just these slight differences in solubility on the part of "insoluble" salts.

CONDITIONS FOR THE COMPLETION OF REACTIONS

Now, finally, in concluding this chapter, we may summarize the conditions, already suggested, which lead reactions toward completion. A reaction will go largely to completion if

1. A solid but slightly soluble is formed — for example, barium sulfate.
2. A large excess of a reactant is added to displace the equilibrium, as in the case of the common-ion effect.
3. Electrovalent compounds react to form at least one but slightly ionized product, as illustrated by a neutralization reaction :



4. At least one of the products is a gas, which escapes. (If the reaction occurs in solution, the gas must be only slightly soluble in the solvent.) The preparation of hydrogen chloride by the action of sulfuric acid on sodium chloride is a good example of this kind.

Questions

1. What is the difference between a static and a dynamic equilibrium?
2. How do you explain the fact that many reactions take place very rapidly in solution which do not take place at all or only slowly when the solid substances are ground together?
3. Given the equation $\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+, \text{OH}^-$, how can you make the reaction move (a) toward the left; (b) toward the right?
4. State Le Chatelier's principle and illustrate it with the effect (a) of increased pressure on a chemical equilibrium and (b) of increased temperature on a chemical equilibrium.
5. Explain the behavior of certain salt hydrates (a) in moist climates and (b) in dry climates.
6. To make ammonia according to the equation $\text{N}_2 + 3 \text{H}_2 \rightleftharpoons 2 \text{NH}_3$, the mixed gases are subjected to high pressure for a good yield. But the temperature is kept below 500° , in spite of the fact that at higher temperatures the velocity of the reactions would be greater. Explain.
7. If a solute is more soluble in a hot solvent than in a cold solvent, is the heat of solution (a) exothermic or (b) endothermic?
8. What is the effect of a catalyst upon a reaction in equilibrium?
9. Derive the expression for the equilibrium constant of the reaction $2A + B \rightleftharpoons 3C + D$.
10. Write expressions for the equilibrium constants of each of the following reactions: (a) $\text{H}_2 + \text{I}_2 \rightleftharpoons 2 \text{HI}$; (b) $2 \text{H}_2 + \text{O}_2 \rightleftharpoons 2 \text{H}_2\text{O}$; (c) $3 \text{H}_2 + \text{N}_2 \rightleftharpoons 2 \text{NH}_3$.

Problems

1. If a certain chemical reaction proceeds at such a rate as to form about 1 g of product per hour at 30° , about how many grams per hour would be formed at 100° ?
2. (a) What is the $[\text{OH}^-]$ of a solution whose $[\text{H}^+] = 10^{-9}$? (b) What is the pH of this solution? (c) Is the solution acid or basic?
3. AgCl is soluble to the extent of about 1×10^{-5} g-mol. wt per liter of water at room temperature. Calculate the solubility product for AgCl ($\text{AgCl} \rightleftharpoons \text{Ag}^+ + \text{Cl}^-$).

4. The solubility of calcium sulfate at 20° is 2.03 g/l, and the saturated solution is ionized to the extent of 52.4 per cent. (a) Express the concentration in terms of gram-molecules per liter. (b) Calculate the gram-molecular concentration of each of the ions and of the nonionized salt. (c) Calculate the value of the solubility product. (d) Calculate the value of the equilibrium constant.

Reading References

ADKINS. "Role of the Catalyst," *Industrial and Engineering Chemistry*, Vol. XXXII, pp. 1189-1192.

BANCROFT. "A Universal Law," *Journal of the American Chemical Society*, Vol. XXXIII, pp. 91-120. A very interesting address, more or less popular in character, showing that the principle of Le Chatelier applies also to fields other than chemistry and physics.

CHAPIN and STEINER. *Second Year College Chemistry*. Chapters XVI, XVII, and XVIII treat of the different kinds of equilibria and the principle of Le Chatelier.

IPATIEFF. "Mixed Catalysts," *Science*, Vol. 91, pp. 605-608.

The Sulfur Family

Introduction. The elements sulfur, selenium, and tellurium, in Group VI of the periodic table (p. 210), bear much the same relation to each other as do chlorine, bromine, and iodine in Group VII. Accordingly, after a detailed description of sulfur and its compounds, we may pass by the much rarer elements selenium and tellurium with brief mention at the end of the chapter.

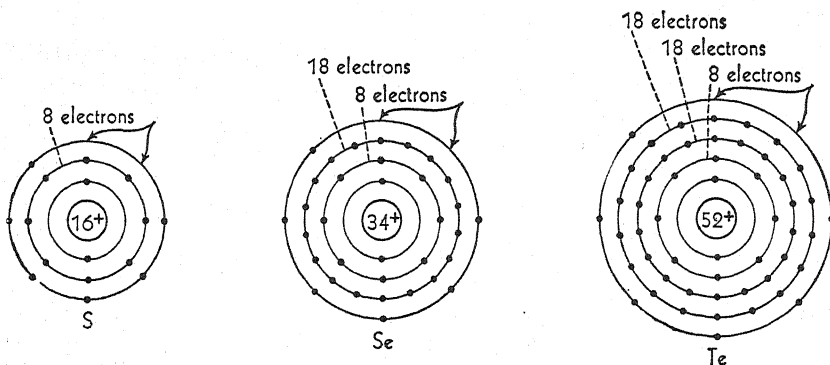


FIG. 212. Diagrams Showing the Distribution of Electrons in the Atoms of the Members of the Sulfur Family. (Arrows indicate unfilled positions)

History and occurrence of sulfur. Sulfur occupied a prominent place among the few elements known to the ancients, and played an important part in the older views concerning the composition of matter. It is the *brimstone* of the Bible.

Free sulfur occurs in many parts of the world, including Sicily, Japan, Spain, Iceland, and Mexico, as well as in different localities in the United States, especially in Texas and Louisiana. Large quantities of sulfur also occur in nature in the compounds known as sulfides and sulfates. Some of the most important of these are the following:

SULFIDES		SULFATES	
Galena	PbS	Gypsum	$\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$
Sphalerite	ZnS	Barite	BaSO_4
Chalcopyrite	CuFeS_2	Celestite	SrSO_4
Pyrite	FeS_2	Epsom salt	$\text{MgSO}_4 \cdot 7 \text{H}_2\text{O}$

Since sulfur is a constituent of some proteins (p. 396), it is present quite generally in vegetable and animal matter, although only in small percentages.

Production and mining of sulfur. The United States produces about 80 per cent of the world's sulfur, almost wholly in Texas. The annual production depends largely upon industrial activity in fertilizers, oil-refining, metal production, and rubber. In favorable years the production is over 2,000,000 tons. Formerly Louisiana produced large amounts, but in 1924 the mine which had yielded more than 10,000,000 tons was closed because of the difficulty of mining. Next to the United States, Sicily produces the most — about 350,000 tons annually. The increasing production of by-product sulfur tends to diminish production from sulfur deposits.

The Frasch process. In Texas and Louisiana the sulfur occurs in large underground deposits covered with quicksand to an extent that makes the ordinary methods of mining impossible. A typical deposit lies at a depth of about 700 ft, is circular in shape, about one-half mile in diameter, and 500 ft in thickness. The problem of how to get this sulfur was finally solved about 1900 by the American engineer Frasch in a very ingenious way.

The principle involved in the Frasch process is shown in Fig. 213. A casing is driven down into the deposit, and inside this are placed two pipes, one inside the other. Water heated under pressure to about 170° is forced down between the casing and the adjacent pipe. The sulfur into which the tubes extend is thereby melted (sulfur melts at about 119°). Hot air is also forced down the innermost tube. This bubbles through the melted sulfur at the bottom of the tube, forming a frothy mixture of relatively low density. The pressure of the air and water forces this mixture up through the space between the two inner pipes to the surface, so that a continuous stream of sulfur flows from the pipe, much as the water from a well. A

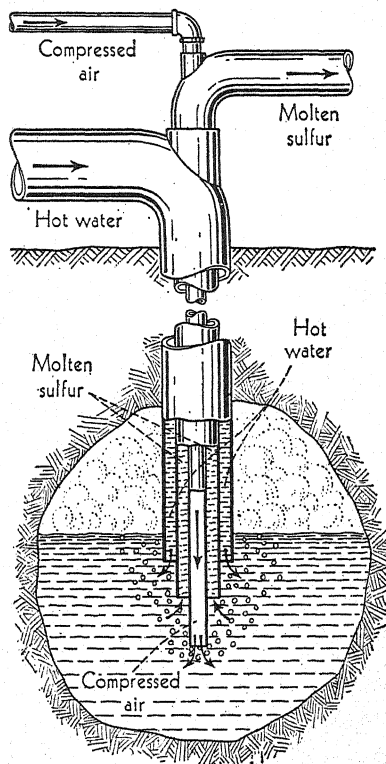


FIG.-213. *Diagram of the Frasch Process*

single well has produced as much as 500 tons of sulfur daily, and the product is 99.5 per cent pure. The production of sulfur in this way is limited only by the market demands.

Methods used in Sicily for purifying the native sulfur. Previous to the development of the Frasch process, most of our free sulfur came

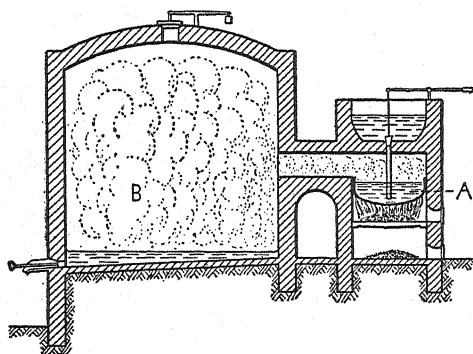


FIG. 214. *Diagram of a Sulfur Still*

from Sicily. The sulfur in the Sicilian deposits is mixed with rock and earthy material and is obtained by heating this mixture. The sulfur melts and drains away from the earthy impurities and is then distilled from an iron retort *A* (Fig. 214), the exit tube of which opens into a cooling chamber *B* of brickwork. When the sulfur vapor first enters the cold chamber, it condenses in the form of a

powder called *flowers of sulfur*. As the chamber becomes warmer, the vapor condenses to a liquid and is drawn off into cylindrical molds, in which it at once solidifies, to form the commercial product called *brimstone*.

Properties. Commercial sulfur is a golden-yellow solid which has no marked taste or odor. It is insoluble in water, but its crystalline forms are soluble in carbon disulfide and in many organic liquids. It melts at 119° into a thin, straw-colored liquid. On further heating, this liquid darkens with increasing viscosity to 200° , then it becomes mobile again but remains dark, and boils at 444.6° . If hot liquid is suddenly chilled (Fig. 215), crystallization is very slow, and it assumes a doughlike form called *plastic sulfur*.

Solid sulfur. Solid sulfur exists in two distinct crystalline forms.

1. **Rhombic sulfur.** Natural crystals and those deposited from solutions of a solvent such as carbon disulfide (CS_2) belong to the rhombic system. The molecule is made up of 8 atoms (Fig. 217).

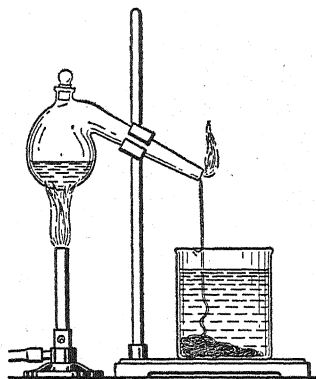


FIG. 215. *Diagram Representing the Preparation of Plastic Sulfur*

2. *Monoclinic sulfur.* From the *melted* state sulfur crystallizes in needles belonging to the monoclinic system. These can be most

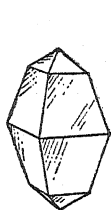


FIG. 216. *Crystal of Rhombic Sulfur*

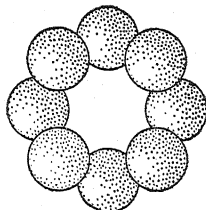


FIG. 217. *Diagram of a Molecule of Rhombic Sulfur (S₈)*

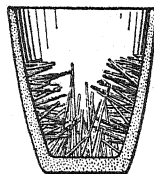


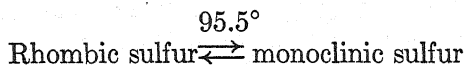
FIG. 218. *Crystals of Monoclinic Sulfur*

readily observed by melting some sulfur in a small crucible, allowing it to cool and partially solidify, then pouring off the remaining liquid. The needle-shaped crystals are found adhering to the bottom and walls of the crucible (Fig. 218).

These two crystalline modifications differ not only in form but in most physical constants as well, such as heat of combustion, density, melting point, and vapor pressure (very small).

CRYSTAL FORM	HEAT OF COMBUSTION	DENSITY	MELTING POINT
Rhombic sulfur	69,300 cal	2.07	112.8°
Monoclinic sulfur	69,360 cal	1.96	119.0°

The transition point. When sulfur crystals form below 95.5°, the rhombic variety is obtained, while above that temperature monoclinic crystals result. At this transition point (p. 260) the two forms of crystals remain unchanged when in contact with each other. If heated above 95.5°, the rhombic form gradually changes into the monoclinic form; if cooled below 95.5°, the reverse change occurs.



The transition temperature closely resembles the freezing point. The one is the temperature of equilibrium between two solid states, the other that between a liquid and a solid.

Chemical conduct. Sulfur combines directly with most of the elements, metals as well as nonmetals, and the resulting binary compounds are called *sulfides*.

1. **Action upon metals.** Most of the metals, when heated with sulfur, combine directly with it, forming metallic sulfides. Sometimes the action is so energetic that the mass becomes incandescent, as in the reaction of iron with sulfur (p. 23). This property recalls the action of oxygen upon metals, and in general it may be said that the metals which combine readily with oxygen are apt to combine easily with sulfur.

2. **Action upon nonmetals.** Under suitable conditions sulfur combines with most of the nonmetals. Thus, with hydrogen it forms the gas hydrogen sulfide (H_2S); with carbon it forms carbon disulfide (CS_2), a heavy, colorless liquid; with chlorine it forms the three chlorides S_2Cl_2 , SCL_2 , and SCL_4 . At ordinary temperatures and in the presence of moisture, sulfur reacts slowly with oxygen, forming sulfuric acid; at higher temperatures it burns, forming the gas sulfur dioxide (SO_2).

3. **Action with oxidizing agents.** When acted upon by oxidizing agents in the presence of water, sulfur is converted first into sulfurous acid and then into sulfuric acid. Since very accurate methods are known for the determination of sulfuric acid, this reaction is the one generally used in estimating the percentage of sulfur present in any substance.

COMPOUNDS OF SULFUR WITH HYDROGEN

By far the most important of these compounds is hydrogen sulfide (H_2S). Compounds having the formulas H_2S_2 , H_2S_3 , and H_2S_5 have also been described; but they are of little importance, and no further reference will be made to them.

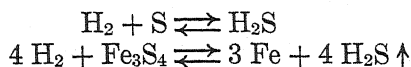
Hydrogen sulfide (H_2S). Hydrogen sulfide is a gas and is often present in the vapors issuing from volcanoes. Dissolved in water, it constitutes the so-called *sulfur waters* of common occurrence. It is formed when organic matter containing sulfur undergoes decay, and the disagreeable odor attending such changes is often partly due to the presence of this gas. The compound is one of our most important laboratory reagents. It is usually prepared as needed, but it can now be purchased compressed in steel cylinders.

Properties. Hydrogen sulfide is a colorless gas having a mild, disagreeable taste and a very offensive odor. It is 1.18 times as heavy as air. The gas may be condensed to a colorless liquid which boils at -59.6° and solidifies at -82.9° . One volume of water at 15° dissolves 4.37 volumes of the gas. By boiling this solution, the

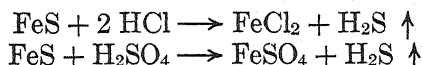
gas is all expelled. In pure form it acts as a violent poison and, even when diluted largely with air, it is very dangerous and causes headache, dizziness, and nausea. Fortunately its marked odor gives warning of its presence.

Preparation of hydrogen sulfide. This gas may be prepared by the two following general methods:

1. **Synthetic method.** When hydrogen is bubbled through boiling sulfur, some of the gas combines directly with the sulfur to form hydrogen sulfide. The latter is likewise formed when hydrogen is passed over certain sulfides heated to the necessary temperature. These reactions are reversible, as is shown in the following equations:

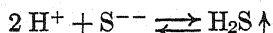


2. **Laboratory method.** Hydrogen sulfide is most conveniently prepared in the laboratory by the action of either dilute sulfuric or hydrochloric acid upon the sulfide of a metal:



Iron sulfide (FeS) is usually employed, although the resulting hydrogen sulfide is not entirely pure. If a greater purity is desired, one may use either sulfide of antimony (Sb_2S_3), which is found in nature in a state of great purity, or sodium sulfide, which can be prepared in the laboratory in a pure condition.

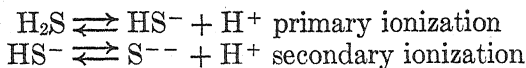
Reason for the reaction. Hydrogen sulfide is very little ionized in solution and is but moderately soluble. Consequently, when an acid is added to a sulfide, the hydrogen ions of the acid and the sulfur ions of the sulfide combine *almost* quantitatively in the equilibrium



The water present soon becomes saturated with the gas, which then escapes as fast as formed, and the reaction continues until either the acid or the sulfide is used up (p. 346).

Apparatus. Iron sulfide is placed in a flask *A* (Fig. 219), and dilute acid is added drop by drop from the separatory funnel *B*. The hydrogen sulfide formed escapes through the tube *C* and is collected in cylinders, as shown in the figure. The Kipp generator (*A*, Fig. 220) is a more convenient form of apparatus for generating the gas in larger quantities.

Chemical conduct of hydrogen sulfide. 1. *Acid properties.* In aqueous solution, hydrogen sulfide is *slightly* ionized. The ionization takes place in two steps:



More ions are furnished by the primary reaction than by the secondary; that is, H_2S is more extensively ionized than HS^- . *This stepwise ionization is characteristic of all acids containing more than one replaceable hydrogen.* The solution of hydrogen sulfide has the general properties of a very weak acid, *hydrosulfuric acid*. It turns blue litmus red and neutralizes bases with the formation of sulfides.

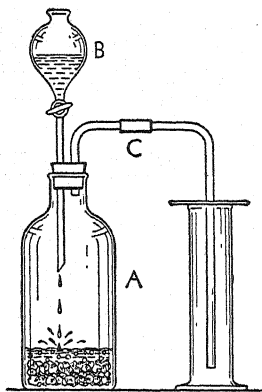
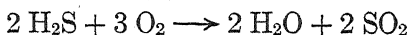


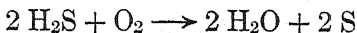
FIG. 219. Diagram of Apparatus for the Preparation of Hydrogen Sulfide

2. *Action of heat.* Heated to a moderately high temperature, or subjected to the action of electric sparks, hydrogen sulfide is decomposed into its elements.

3. *Action of oxygen.* If a solution of hydrogen sulfide in water (hydrosulfuric acid) is exposed to air, the hydrogen of the sulfide slowly unites with oxygen to form water, while sulfur separates as a solid. In this way are formed the sulfur deposits found about sulfur springs. Hydrogen sulfide is readily inflammable and burns in either oxygen or air, according to the equation



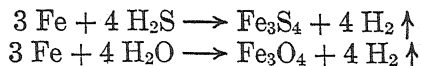
When there is not sufficient oxygen to combine with both the sulfur and the hydrogen, the latter element combines with the oxygen, and the sulfur is set free:



4. *Reducing action.* Because of the ease with which its hydrogen is given up in contact with an oxidizing agent, hydrogen sulfide acts as a strong *reducing agent*. For example, if it is bubbled through concentrated nitric or sulfuric acid, both of which are strong oxidizing agents, the sulfur of the sulfide is oxidized to form free sulfur, and the acid is at the same time partially reduced.

5. *Action upon metals.* The action of hydrogen sulfide upon a number of the metals is very similar to that of water under like

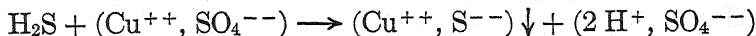
conditions, and results in the displacement of its hydrogen by the metal. Thus, when hydrogen sulfide or steam is passed over iron filings heated in a tube, the reactions are as follows :



Salts of hydrosulfuric acid; sulfides. The salts of hydrosulfuric acid, the metallic *sulfides*, are an important class of compounds. They are all solids; most of them are insoluble in water, while some are insoluble even in acids. As prepared in the laboratory, some of these salts, such as copper sulfide (CuS) and silver sulfide (Ag_2S), are black; others, as cadmium sulfide (CdS) and arsenic sulfide (As_2S_3), are yellow; while zinc sulfide (ZnS) is white. Many of these sulfides are found in nature, and some of them are the compounds from which the metals are obtained on an industrial scale. They will be mentioned frequently in connection with the metals. Sulfur combines with many nonmetals, such as carbon and phosphorus, to form sulfides. These are not salts, but are covalent compounds.

Preparation of the sulfides. The soluble sulfides, like those of sodium and potassium, are most readily prepared by treating the respective hydroxides of these metals with hydrosulfuric acid. Both the acid and normal salts may be obtained in this way.

The insoluble sulfides may be prepared by heating the metals with sulfur, although the more convenient method consists in passing hydrogen sulfide into aqueous solutions of metallic compounds. Thus, copper sulfide may be easily prepared by dissolving copper sulfate (CuSO_4) in water and passing hydrogen sulfide into the solution. The insoluble copper sulfide precipitates as fast as formed, and may be removed from the liquid by filtration. The reaction which takes place is expressed in the equation



Precipitation of sulfides. The precipitation of sulfides as carried out in the laboratory may be illustrated as follows: Hydrogen sulfide is generated in a Kipp apparatus *A* (Fig. 220) and is passed successively into bottles *B*, *C*, *D*, *E*, containing, respectively, the aqueous solutions of silver nitrate, cadmium sulfate, zinc acetate, and sodium hydroxide. As the gas bubbles through the solutions, there is formed black silver sulfide (Ag_2S) in *B*, yellow cadmium sulfide (CdS) in *C*, white zinc sulfide (ZnS) in *D*. No precipitate is produced in *E*, for, although sodium sulfide is formed, it is soluble in water and therefore does not separate. Reactions of this kind are of great importance in chemical analysis.

The persulfides. The persulfides of sodium, potassium, and calcium are formed, together with other products, when aqueous solutions of the hy-

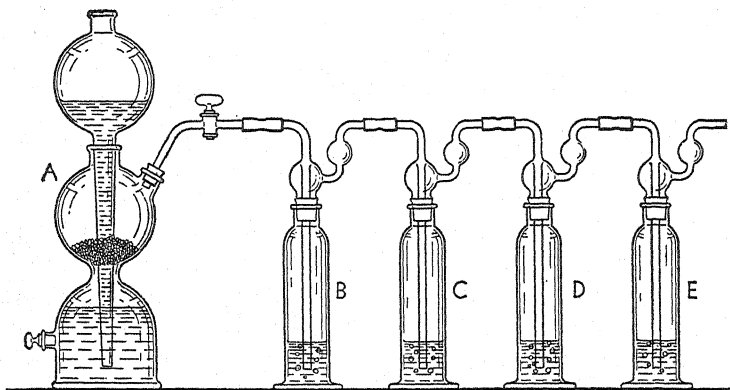


FIG. 220. Diagram of Apparatus Used in the Precipitation of Insoluble Sulfides

droxides of these metals are heated with sulfur. The exact composition of these persulfides is not known with certainty. They are all unstable, and readily decompose into the ordinary sulfides and free sulfur. Some of the persulfides are used as insecticides because the liberated sulfur is effective for this purpose. The *lime-sulfur spray* that is being used so extensively at present for destroying insects injurious to trees is a red solution formed by heating calcium hydroxide with sulfur and water; among other compounds it contains calcium persulfide (probably a mixture of CaS_4 and CaS_5).

OXIDES AND OXYGEN ACIDS OF SULFUR

With oxygen, sulfur forms the following compounds:

Sulfur dioxide (SO_2), a colorless gas.

Sulfur trioxide (SO_3), a colorless liquid boiling at 44.6° .

Sulfur sesquioxide (S_2O_3), a bluish-green crystalline solid.

Sulfur heptoxide (S_2O_7), a viscous liquid.

Of these oxides the first two are by far the most important and best known. They are both *acid anhydrides* and combine with water to form sulfurous acid and sulfuric acid respectively.

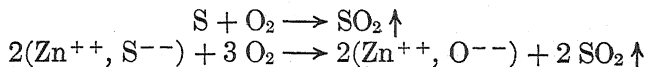
Sulfur dioxide (sulfurous anhydride) (SO_2). This is the well-known gas resulting from the combustion of sulfur. It was first obtained in the pure state and recognized as a definite compound by Priestley in 1775. It occurs in nature in the gas issuing from volcanoes and in solution in the waters of some springs.

Properties. Sulfur dioxide is a colorless gas and has the peculiar irritating odor so noticeable when sulfur is burned. It is a heavy

gas, 2.2 times as heavy as air. Under standard conditions 1 volume of water dissolves 79.79 volumes of the gas. It is easily condensed (Fig. 221) to a colorless liquid that boils at -10° and freezes to a snowlike solid that melts at -75.5° . Liquid sulfur dioxide is sold in small steel containers or in tank-car lots for use as a bleach and in some mechanical refrigerators (p. 124).

Preparation. Sulfur dioxide is prepared by the three following general methods:

1. *By the combustion of sulfur or a metallic sulfide.* In either case the sulfur is converted into sulfur dioxide:

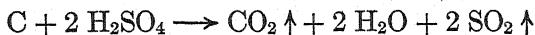


The enormous quantities of sulfur dioxide used in the manufacture of sulfuric acid are prepared by this general method.

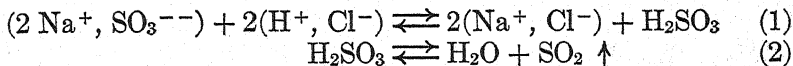
2. *By the reduction of sulfuric acid.* When concentrated sulfuric acid is heated with certain metals, such as copper, a part of the acid is reduced to sulfurous acid. The latter compound then decomposes into sulfur dioxide and water. The steps of the reaction are given on page 367, but the complete equation is as follows:



A similar reaction takes place when carbon is heated with sulfuric acid:



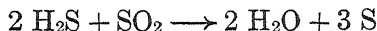
3. *By the action of acids upon a sulfite.* Sulfites are salts of sulfurous acid (H_2SO_3). When an acid, such as hydrochloric acid, is added to a sulfite, sulfurous acid is formed, which decomposes into water and sulfur dioxide. The reactions are expressed in the following equations:



Explanation of the reaction. In the action of hydrochloric acid upon sodium sulfite, as expressed in these equations, we have two reversible reactions depending upon each other. It might be expected that the reaction expressed in equation (1) would result in an equilibrium, since none of the substances represented in the equation is insoluble or volatile in the presence of water. The sulfurous acid, however, decomposes as fast as it forms, according to equation (2), and the resulting sulfur dioxide escapes in the form of a gas. The reaction continues, therefore, until practically

all the sodium sulfite has reacted. Since sulfur dioxide is quite soluble in water, it is evident that the reaction should be carried out in the presence of as little water as possible.

Chemical conduct. Sulfur dioxide is an active substance chemically. It combines directly with chlorine to form *sulfuryl chloride*, SO_2Cl_2 ; with water to form *sulfurous acid*, H_2SO_3 ; and with many other substances. Toward oxygen it acts as a reducing agent, being oxidized to sulfur trioxide, SO_3 . Toward certain hydrogen compounds it acts as an oxidizing agent, as shown in the following equation:



Many *not too stable* oxides of lower valence act in this same way, either as reducing agents or as oxidizing agents. They are oxidizing agents because they are unstable and give up oxygen readily; they are reducing agents because they tend to take up oxygen and pass to a higher, more stable valence.

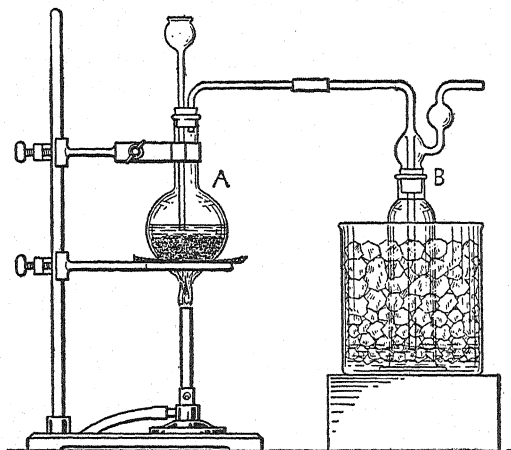
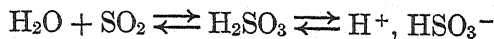


FIG. 221. Liquefaction of Sulfur Dioxide May Be Accomplished by Generating the Gas in Flask A and Conducting It into a Vessel B Surrounded by a Freezing Mixture of Ice and Salt

Sulfurous acid (H_2SO_3)

When sulfur dioxide is passed into water, some of the gas combines with water to form sulfurous acid (H_2SO_3), while the remainder is held in a state of solution. The sulfurous acid formed is in equilibrium, on the one hand with water and dissolved sulfur dioxide,

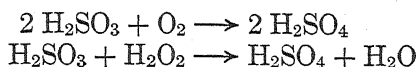
and on the other hand with the ions H^+ and HSO_3^- , resulting from the partial ionization of the acid:



If this liquid is heated, it gives off sulfur dioxide and acts as if it were simply a solution of sulfur dioxide in water. Toward a base, on the other hand, it acts as a solution of sulfurous acid, but the acid can be obtained only in the form of a dilute solution. This solution has the following properties:

1. *Acid properties.* In aqueous solutions the compound forms the ions H^+ and HSO_3^- . Some of the latter ions dissociate further into the ions H^+ and SO_3^{--} ; the more dilute the solution, the more extensive is this secondary ionization. The solution has all the properties of a weak acid.

2. *Reducing properties.* Sulfurous acid is a good reducing agent; it takes up oxygen either from the air or from unstable substances containing oxygen, and changes into sulfuric acid, thus:



In this reducing property it resembles its anhydride SO_2 .

Because of this tendency of sulfurous acid to combine with oxygen, a solution of the acid always contains some sulfuric acid, unless freshly prepared. The speed of the reaction by which sulfurous acid is changed into sulfuric acid is greatly diminished in the presence of a trace of sugar or glycerin, which acts as a negative catalyst (p. 172).

3. *Bleaching properties.* Sulfurous acid acts upon many organic dyes and changes them into colorless compounds. It is therefore useful as a bleaching agent, especially for such substances as paper and straw goods, the texture of which would be injured by a more powerful bleaching agent, such as chlorine.

Illustration. The bleaching properties of sulfurous acid may be shown by bringing a small dish of burning sulfur under a bell jar (Fig. 222) in which has been placed some highly colored flower thoroughly moistened with water. The sulfur dioxide combines with the moisture to form sulfurous acid, which slowly bleaches the flower. The reactions involved in these changes are not thoroughly understood. In some cases the sulfur dioxide apparently combines directly with the coloring matter to form unstable colorless compounds. In other cases the bleaching properties seem to be due to the reducing action of sulfurous acid.

4. *Antiseptic and preservative properties.* Sulfurous acid destroys many microorganisms and may therefore be used as a preservative, to prevent such changes as putrefaction and fermentation, which are caused by these organisms.

Uses of sulfurous acid. Sulfurous acid is used mainly in the preparation of sulfites and as a bleaching agent and preservative. Formerly it was often used for disinfecting rooms after the occurrence of contagious diseases, but it is now largely replaced by more effective reagents. Both as a preservative and as a bleaching agent it is

used to a considerable extent with certain foods, such as canned corn, dried fruits, sirups, and wines. Whether or not this use should be permitted is a much-debated question.

Salts of sulfurous acid; sulfites. Being dibasic, sulfurous acid forms both acid and normal salts. Thus, with sodium it forms the salts NaHSO_3 and Na_2SO_3 . With the exception of the sulfites of sodium and potassium, the normal sulfites are either insoluble in water or nearly so, while the acid sulfites are soluble. The normal salts can be prepared either by the action of sulfurous acid upon the hydroxides of the metals or by the general precipitation method used for preparing insoluble compounds. The sulfites are all solid substances and, like sulfurous acid itself, combine readily with oxygen, forming the corresponding sulfates. They are therefore good reducing agents. Because of this property, unless freshly prepared, they are apt to contain some of the corresponding

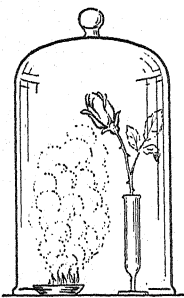
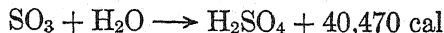


FIG. 222. *Bleaching a Flower with Sulfur Dioxide*

sulfates. Calcium acid sulfite is largely used in the manufacture of paper from wood, since it dissolves the objectionable constituent (lignin) of the wood, leaving the pure cellulose.

Sulfur trioxide (sulfuric anhydride) (SO_3). Sulfur trioxide is a colorless liquid which solidifies at 16.83° and boils at 44.6° . A trace of moisture causes it to solidify into a mass of silky white crystals. Toward a substance having a strong affinity for oxygen, sulfur trioxide acts as an oxidizing agent, giving up one third of its oxygen and being reduced to sulfur dioxide. In contact with the air, sulfur trioxide fumes strongly; and it dissolves in water, with the liberation of a great deal of heat. The product of this reaction is sulfuric acid; so sulfur trioxide is the *anhydride* of that acid:



Preparation of sulfur trioxide. When sulfur is burned in oxygen, minute quantities of sulfur trioxide are formed with the sulfur dioxide. When sulfur dioxide and oxygen are heated together, combination takes place; but the speed of the reaction is so slow that only traces of the trioxide result. In the presence of a catalyst, such as finely divided platinum, the speed is greatly increased; in this way sulfur trioxide can be obtained in quantities (Fig. 223). The reaction is reversible, as indicated in the following equation:



The largest yield of sulfur trioxide is obtained when the reaction is carried out at approximately 400° ; at this temperature about 98 per cent of the sulfur dioxide combines with oxygen.

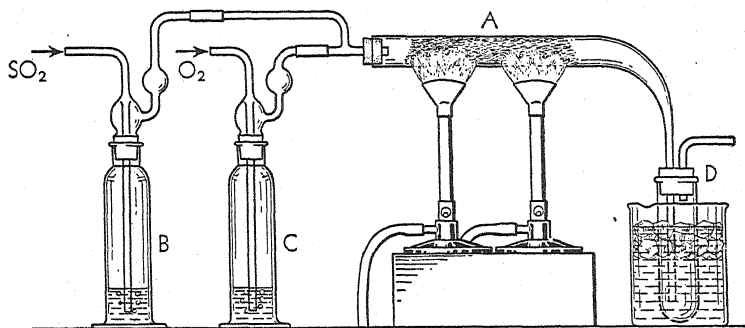


FIG. 223. *Laboratory Apparatus Used in the Preparation of Solid Sulfur Trioxide*

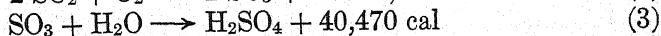
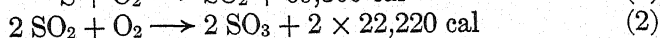
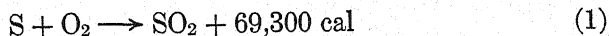
The gases are dried by bubbling them through concentrated sulfuric acid in B and C. A is the catalyst. The gas is condensed in tube D cooled by ice water

Sulfuric acid (H_2SO_4). Sulfuric acid has long been known, and was one of the most important reagents employed by the later alchemists. Not only is it one of the most common reagents in the laboratory, but enormous quantities of it are consumed in the industries. It would be hard to name any one chemical compound of more fundamental importance in the arts and industries.

Properties. Pure anhydrous sulfuric acid, or *hydrogen sulfate*, is a colorless, oily liquid. Because of its oily consistency, together with the fact that it was formerly obtained by distilling the (partially oxidized) sulfate of iron known as green vitriol, it is often called *oil of vitriol*. Its density is 1.834 at 20° . When heated to 330° it boils, and a portion of the compound decomposes into sulfur trioxide and water in the process. At a low temperature hydrogen sulfate forms crystals which melt at 10.49° .

Manufacture of sulfuric acid. Two general methods for the manufacture of sulfuric acid are in use at the present time. The newer one of these is known as the *contact* process, while the older one is called the *lead-chamber* process.

1. **Contact process.** The reactions taking place in this process are represented by the following equations:



Sulfur dioxide is prepared according to equation (1), by burning sulfur or some sulfide, such as iron pyrite (FeS_2), in air. The resulting sulfur dioxide, together with sufficient air to furnish the necessary oxygen, is conducted through iron tubes filled with some porous material (asbestos or magnesium sulfate), through which a suitable catalyst is interspersed. The catalyst and its support are kept at about 400° . Under these conditions sulfur trioxide is formed according to equation (2). The resulting sulfur trioxide is then brought into contact with concentrated sulfuric acid and combines with the water present in the acid to form more sulfuric acid.

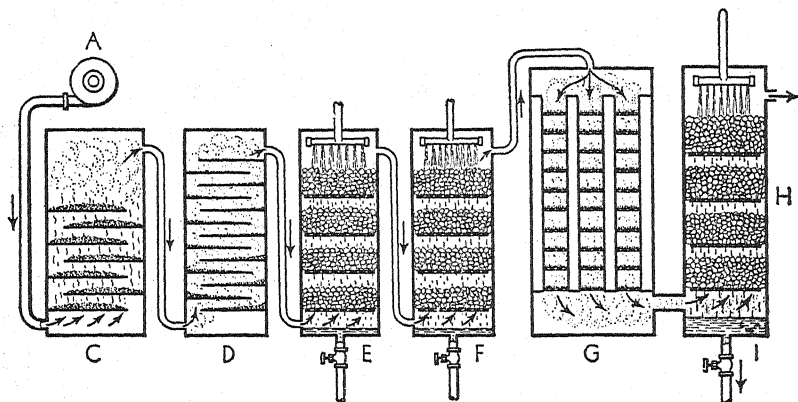


FIG. 224. Diagram to Illustrate the Commercial Preparation of Sulfuric Acid by the Contact Process

The sulfur in the chamber *C* is burned by the air forced into the chamber by the blower *A*. The resulting sulfur dioxide and oxygen (air) are freed from dust by passing through the chambers *D* and *E* and dried by a spray of sulfuric acid in *F*. The gases are then passed over the catalyzer in *G*, where sulfur trioxide is formed by the union of the sulfur dioxide and oxygen. The resulting sulfur trioxide is absorbed in the chamber *H*, by means of concentrated sulfuric acid, and the resulting product drawn off at *I*.

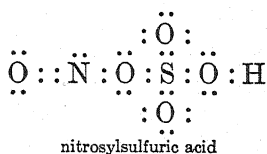
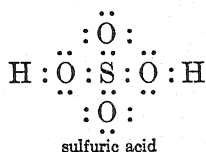
Historical. The only part of the process which is difficult to carry out on a commercial scale is the formation of the sulfur trioxide. It has long been known that sulfur dioxide and oxygen combine when passed over finely divided platinum, but the cost of platinum, together with the poor yield of sulfur trioxide obtained, had made the process an impracticable one. A study of the conditions under which the reaction takes place resulted in improvements in the process, until finally, in 1901, the German chemist Knietzsch succeeded in overcoming the difficulties to such an extent as to make the process a commercial success for the manufacture of the pure concentrated acid. While platinum is a very effective catalyst for the process, it is very expensive; its commercial value is greater than

that of gold. This has led to the use of other catalysts, among which compounds of vanadium and iron oxide appear to be the best.

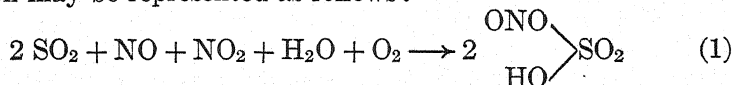
Some of the more important conditions necessary for making the process a success were found to be the following: (1) The sulfur dioxide and air must be free from dust particles and other impurities, such as the traces of oxides of arsenic which are likely to be formed if iron pyrite or other sulfides are the source of the dioxide used in the process; otherwise the catalyst loses its power. (2) An excess of oxygen over that required in the second equation must be present. (3) The temperature must be maintained at about 400°. (4) A spray of sulfuric acid containing from 2 to 3 per cent of water must be used for absorbing the sulfur trioxide, since the latter will not combine rapidly with pure water.

2. Lead-chamber process. This process receives its name from the fact that the reactions are carried out in large sheet-lead chambers. The following substances enter into the reaction: (1) sulfur dioxide obtained as in the contact process; (2) a mixture of nitric oxide and nitrogen dioxide; (3) water in the form of steam; (4) oxygen (air). These four substances are introduced in the proper proportions into large sheet-lead chambers, and under suitable conditions they react to form sulfuric acid. The reactions involved are quite complex, and are not thoroughly understood. It is probable that the two following general reactions take place:

1. The substances introduced into the chambers first react to form a derivative of sulfuric acid known as *nitrosylsulfuric acid*. The relation of these two compounds to each other may be seen from their structural formulas:

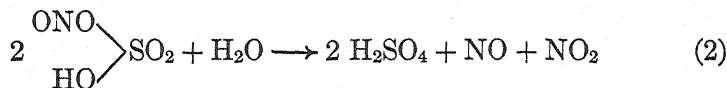


Nitrosylsulfuric acid differs from sulfuric acid in composition by containing the univalent group (or *radical*) NO (called the *nitrosyl group*) in place of one of the hydrogen atoms of sulfuric acid. Its formation may be represented as follows:



This acid can be obtained in the form of white crystals called *chamber crystals*.

2. In the commercial manufacture of sulfuric acid, however, these crystals do not form, because the steam changes the nitrosyl acid into sulfuric acid as fast as it is formed :



The sulfuric acid collects upon the floor of the chambers in the form of an aqueous solution containing from 62 to 70 per cent of acid. This product is called *chamber acid* and is impure; but for many purposes, such as the manufacture of fertilizers, it needs no further treatment. It can be concentrated by evaporation in open pans made of cast iron, lead, or silica, upon which the acid has little or no action.

It will be noted that in reaction (2) the same quantities of the oxides of nitrogen are formed as are required for reaction (1). Theoretically, therefore, a small amount of these oxides should suffice to prepare an unlimited amount of sulfuric acid; practically, some of the oxides are lost, and this loss must be replaced.

The lead-chamber plant. The simpler parts of such a plant for the manufacture of sulfuric acid are illustrated in Fig. 225. Sulfur, or some sulfide such as FeS_2 , is burned in the furnace *A*. The resulting sulfur dioxide, together with the necessary amount of air, passes into the structure *C*, known as the *Glover tower*. In it the oxides of nitrogen are generated, as will be explained later, and these, together with the sulfur dioxide and air, pass into the chambers *D*, *D*. Water or steam is also introduced into these chambers at suitable points. Here the reactions take place which result in the formation of the sulfuric acid. The nitrogen remaining after the withdrawal of the oxygen from the air which entered the chamber escapes through the structure *E*, known as the *Gay-Lussac tower*. In order to prevent the escape of the nitrogen dioxide regenerated in the reaction, this tower is filled with pieces of acid-resisting rock or coke over which trickles concentrated sulfuric acid admitted in the form of a spray (*F*) at the top. The concentrated acid absorbs the nitrogen dioxide but not the nitric oxide, so that the latter escapes along with the nitrogen. The acid which is sprayed into the top of the tower collects in the bottom and is run off into the vessel *G*, from which it is forced into the tank at the top of the Glover tower *C*. Here it is mixed with some dilute sulfuric acid, and the mixture sprayed into the top of the tower, which is partly filled with some acid-resisting rock. As the acid passes down through this material, it meets with the hot gases entering from the furnace, whereby the nitrogen dioxide is liberated from the acid, passes over into the chamber *D*, and again enters into the reaction. During the process just described the dilute acid becomes sufficiently concentrated to serve again as an absorbent of

nitrogen dioxide. The necessary quantity of it is therefore run into the vessel *H* from the bottom of the tower, and then forced into the tank

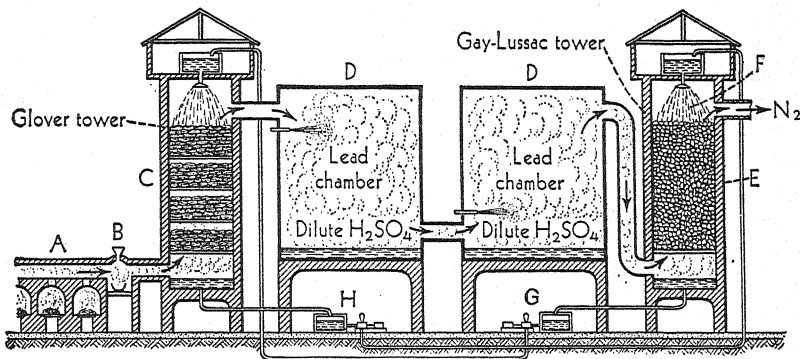


FIG. 225. Diagram to Illustrate the Lead-Chamber Process for the Manufacture of Sulfuric Acid

at the top of *E*. In order to replace the oxides of nitrogen lost in the process, the necessary quantity is generated in vessel *B*. The sulfuric acid formed collects in the bottom of the chambers and is drawn off from time to time.

Historical. The chamber process dates back to the year 1746. For a number of years previous to this date sulfuric acid had been made by burning sulfur mixed with potassium nitrate in large glass globes. Since these globes were very fragile, and since lead was known to be acted upon to but a very slight extent by the dilute acid, Dr. Roebuck, an Englishman, suggested the substitution of lead-lined chambers for the glass globes. The first plant for the manufacture of the acid by this method was constructed in Birmingham, England.

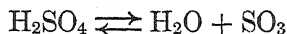
Relative advantages of the contact process and lead-chamber process. It will be noted that in the contact process it is just as easy to prepare the pure concentrated acid as the dilute acid. In the chamber process the dilute acid is obtained first and can be prepared at a very low cost. It is used almost exclusively in making fertilizers. The concentration and purification of the dilute acid is an expensive operation, and therefore the contact process is best adapted for the manufacture of the concentrated acid.

By-product sulfur dioxide. The sulfides of some of the metals, such as zinc, copper, and lead, constitute the ores from which these metals are largely obtained. In the extraction of the metals it is often found most convenient first to convert the sulfides into oxides by heating them in the air. The resulting sulfur dioxide may be utilized in the manufacture of sulfuric acid, especially in countries where the cost of sulfur is high. It often happens, therefore, that the manufacture of sulfuric acid is carried on in connection with the separation of metals from their ores.

Radicals. It should be noticed that on page 363 the univalent nitrosyl group, —NO , was called a *radical*; and the question naturally arises, What is the distinction between an ion such as NH_4^+ or OH^- and the univalent radical NO ?

In the structural formula for nitrosylsulfuric acid, the NO group is represented as attached to an oxygen atom by a *covalent* bond, whereas ions form *electrovalent* bonds. We may define a radical as a group of two (or more) atoms that as a group form a covalent bond with another atom. The same group, such as OH , may act as an ion in one compound (Na^+ , OH^-) and as a radical in others (H—OH or $\text{H}_3\text{C—OH}$).

Chemical conduct of hydrogen sulfate and of sulfuric acid. Pure hydrogen sulfate is a strong oxidizing agent and is extremely corrosive. When it is heated above 100° , dissociation into water and sulfur trioxide begins. The sulfur trioxide escapes to a greater extent than does the water, until the residual liquid contains 1.67 per cent of water. The resulting mixture then distills at 338° with unchanged concentration (p. 257). If the vapor is heated further, dissociation gradually increases until, at about 450° , it is complete. The reaction is reversible, and recombination of the water and sulfur trioxide takes place as the temperature falls:



Hydrogen sulfate mixes with water in all proportions, evolves a large amount of heat, and forms sulfuric acid.

The chemical conduct of the acid may be described as follows:

1. **Acid properties.** In concentrated aqueous solutions hydrogen sulfate forms the ions H^+ and HSO_4^- ; and the latter, on further dilution of the solution, breaks down into the ions H^+ and SO_4^{--} . It is this aqueous solution containing hydrogen ions which is properly termed sulfuric acid. In a *normal solution* of hydrogen sulfate, 51 per cent of its hydrogen acts as free ions.

2. **Action as an oxidizing agent.** Sulfuric acid parts with one fourth of its oxygen rather easily and, in concentrated form, is a very good oxidizing agent. When heated with metals, sulfur, carbon, or various other oxidizable substances, sulfuric acid acts virtually as though it gave up nascent oxygen according to the equation



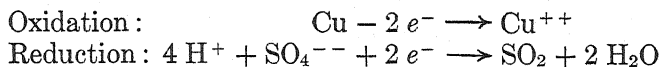
3. **Action on metals.** A *dilute solution* of sulfuric acid acts upon the metals that precede hydrogen in the electromotive series (p. 277) to form a sulfate of the metal and liberate hydrogen. Such a solution

has no action upon the metals that follow hydrogen in the series, save as the oxygen of the air first oxidizes the metal.

On the other hand, the *concentrated* acid acts upon a number of the metals without respect to their position in the electromotive series; but in all these cases the action results in the reduction of a part of the acid. Such reactions apparently involve two processes, for which separate equations may be written. The addition of these *ion-electron* equations gives the completed equation. With copper the equation representing the reaction is



To visualize better the changes which have taken place, the molecular equation may be broken down into an oxidation equation and a reduction equation:



Since the same number of electrons is lost in the first equation as is gained in the second, the two ion-electron equations may be added to give the ionic equation

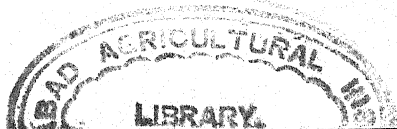


4. Action on salts. We have repeatedly seen that when a salt of a low-boiling acid is heated with an acid having a high boiling point, the low-boiling acid is liberated from its salt and driven out as a gas or vapor (p. 291). Now sulfuric acid has a higher boiling point than that of any of the common acids, and, being an inexpensive compound, *it is admirably adapted to the preparation of other acids from their salts.*

5. Action on water. When the concentrated acid is mixed with water, a marked contraction in volume takes place. Moreover, the process is attended by the evolution of a large amount of heat, which may even be sufficient to cause the liquid to boil. Care must therefore be taken, in mixing the acid with water, to keep the solution thoroughly stirred during the process, and to pour the acid into the water, not the reverse.

When hydrogen sulfate and water are mixed in molecular proportions — namely, 98 parts by weight of the sulfate to 18 of water — and the resulting solution is cooled, the two unite to form the hydrate $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$. This is a white crystalline substance melting at 8.62° .

6. Action on organic substances. Not only can sulfuric acid combine with water, but it will often withdraw the elements hydrogen



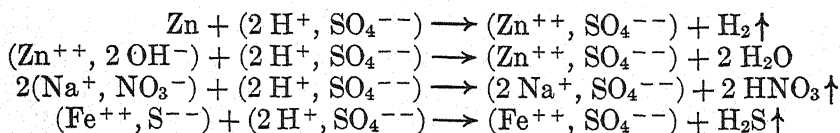
and oxygen from a compound containing them, decomposing the compound and combining with the water so formed. For this reason most organic substances, such as sugar, wood, cotton and woolen fiber, and even animal tissues, all of which contain much oxygen and hydrogen in addition to carbon, are decomposed by the concentrated acid, leaving the black carbon as a residue.

The production and uses of sulfuric acid. The annual production of sulfuric acid in the United States fluctuates widely but averages about 7,000,000 tons calculated as 100 per cent H_2SO_4 . The fertilizer industry consumes approximately one third of the output. Large amounts are consumed in the refining of petroleum and coal-tar products; in the cleaning of scale from iron and steel; and in the manufacture of chemicals. Its minor uses are innumerable.

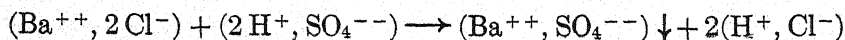
Salts of sulfuric acid; sulfates. The sulfates constitute a very important class of compounds, and many of them have extensive commercial uses. The normal salts are all solids and, with the exception of those of barium, strontium, and lead, are soluble in water. Two others, namely, calcium sulfate and silver sulfate, are only slightly soluble. The hydrates of many of the sulfates are more frequently used than the anhydrous salts. Some of the more important of these compounds are included in the following table:

FORMULA	CHEMICAL NAME	COMMON NAME
$\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$	Hydrate of sodium sulfate	Glauber's salt
$\text{MgSO}_4 \cdot 7 \text{H}_2\text{O}$	Hydrate of magnesium sulfate	Epsom salt
$\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$	Hydrate of calcium sulfate	Gypsum
$\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$	Hydrate of copper sulfate	Blue vitriol, or bluestone
$\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$	Hydrate of iron sulfate	Green vitriol, or copperas
$\text{ZnSO}_4 \cdot 7 \text{H}_2\text{O}$	Hydrate of zinc sulfate	White vitriol
BaSO_4	Barium sulfate	Barite, or heavy spar

The sulfates can be prepared by the action of sulfuric acid upon the metals, their oxides and hydroxides, and many of their salts, as illustrated by the following equations:



The insoluble sulfates may be prepared by precipitation. Thus, barium chloride (BaCl_2) and sulfuric acid in aqueous solutions react:



The resulting barium sulfate separates in the form of a white solid. Since only soluble sulfates and sulfuric acid yield the ion SO_4^{--} in solution, this reaction serves as a delicate test for these compounds.

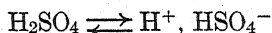
Other oxygen acids of sulfur. In addition to sulfurous and sulfuric acids a number of other oxygen acids of sulfur are known, either in the free state or in the form of their salts. The formulas and names of the most important of these are as follows:

Thiosulfuric acid	$\text{H}_2\text{S}_2\text{O}_3$	Dithionic acid	$\text{H}_2\text{S}_2\text{O}_6$
Hyposulfurous acid	$\text{H}_2\text{S}_2\text{O}_4$	Trithionic acid	$\text{H}_2\text{S}_3\text{O}_6$
Pyrosulfuric acid	$\text{H}_2\text{S}_2\text{O}_7$	Tetrathionic acid	$\text{H}_2\text{S}_4\text{O}_6$
Persulfuric acid	$\text{H}_2\text{S}_2\text{O}_8$	Pentathionic acid	$\text{H}_2\text{S}_5\text{O}_6$

The thionic acids derive their names from a Greek word meaning "sulfur." With the exception of pyrosulfuric acid, these acids are so unstable that they have been obtained only in dilute aqueous solution or in the form of salts. A brief discussion of pyrosulfuric and persulfuric acid follows.

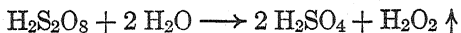
Pyrosulfuric acid ($\text{H}_2\text{S}_2\text{O}_7$). Sulfur trioxide dissolves in sulfuric acid in all proportions, forming *fuming sulfuric acid*, often called *oleum*. This acid is of especial importance in the manufacture of dyes. If the sulfur trioxide and sulfuric acid are mixed in molecular proportions, the two combine to form a solid crystalline compound, $\text{H}_2\text{S}_2\text{O}_7$, known as *pyrosulfuric acid*.

Persulfuric acid ($\text{H}_2\text{S}_2\text{O}_8$). This acid is sometimes called *perdisulfuric acid* to distinguish it from a similar acid of the formula H_2SO_5 , called *permonosulfuric acid*, or *Caro's acid*. It will be recalled that in concentrated solutions of sulfuric acid there exists the equilibrium expressed in the following equation:



When such solutions are electrolyzed, hydrogen is evolved at the cathode. At the anode the ions HSO_4^- are discharged, and under certain conditions the resulting radicals combine to form the compound $(\text{HSO}_4)_2$, or $\text{H}_2\text{S}_2\text{O}_8$, which remains dissolved in the liquid about the anode, giving the ions 2H^+ , $\text{S}_2\text{O}_8^{--}$. This compound is known as *persulfuric acid*. While the acid is unstable and exists only in dilute solution, its salts can be obtained in pure condition. They are prepared by the electrolysis of concentrated solutions of the corresponding acid sulfates. For example, a concentrated solution of potassium hydrogen sulfate, upon electrolysis, yields persulfuric ions at the anode, just as does the electrolysis of sulfuric acid itself. With increasing concentration the solubility product is reached (p. 343), and the persulfate ions, together with the potassium ions, leave the solution as crystals of the salt $\text{K}_2\text{S}_2\text{O}_8$.

Persulfuric acid, as well as its salts, is a strong oxidizing agent. Vacuum distillation of solutions of persulfuric acid or its ammonium salt yields hydrogen peroxide:



Sulfur monochloride (S_2Cl_2). This is the best-known chloride of sulfur. It was formerly thought to have the formula SCl , whence the name *monochloride*. It is formed when chlorine is passed over heated sulfur, and is a yellow oily liquid boiling at 138° and having an extremely disagreeable odor. It is a good solvent for sulfur, and this solution is used in vulcanizing rubber. Large amounts have been used in the manufacture of the poison compound known as "mustard gas."

SELENIUM AND TELLURIUM

The elements *selenium* and *tellurium* should be briefly described along with sulfur, since the three elements constitute a periodic family. Selenium resembles sulfur in many of its properties, as well as in its chemical conduct. While tellurium does not show this marked similarity, nevertheless its compounds are closely related in composition to those of sulfur.

Tellurium was discovered by Reichenstein and Klaproth toward the end of the eighteenth century. The latter investigator gave to the element the name it now bears, the word meaning "the earth." A few years later (1817) Berzelius isolated a new element, which he named selenium, from a Greek word meaning "the moon." Both these elements occur in nature in the free state as well as in combined condition, but only in comparatively small quantities, far less abundantly than sulfur.

Selenium. This element is frequently found in small quantities in natural sulfur. Combined with metals it also occurs along with some of the sulfides, especially pyrite (FeS_2). When sulfur or a sulfide containing selenium is used in the manufacture of sulfuric acid, some free selenium is always found in the flue dust, as well as in the slime collecting in the bottom of the lead chambers; and it was from this material that Berzelius first isolated the element. Occasionally compounds of selenium occur in the soil and are absorbed by certain varieties of plants. Cattle and sheep feeding on these plants are poisoned, and thousands have died from this poisoning. The symptoms have been called blind staggers, or alkali poisoning. This is a rare instance of the absorption of mineral matter by plants, with the acquisition of poisonous properties by the plants.

Properties. Selenium resembles sulfur in that it occurs in a number of different forms, although the relation of these to each other has not been so well determined as in the case of sulfur. It is a conductor of electricity, and *its conductivity increases with the intensity of the light* to which the selenium is subjected. When heated in the presence of air, it forms selenium dioxide (SeO_2).

Considerable selenium is recovered each year in the United States as a by-product in the refining of copper, and more could be produced if there were a large demand for it. At present about the only use for it is in certain electrical appliances (rectifiers and light-sensitive cells), and for making red glass and decolorizing green glass. To some extent it is used as a covering for flameproofing electric-switchboard cables and in insecticides.

Compounds of selenium. In general it may be stated that the compounds of selenium resemble those of sulfur, in composition as well as in general properties.

The most important of these compounds are as follows: (1) *hydrogen selenide* (H_2Se), a gas of unbearable odor; (2) *selenium dioxide* (SeO_2), a white crystalline solid formed by burning selenium in air; (3) *hydrogen selenite* (H_2SeO_3), an unstable white crystalline solid formed by the combination of selenium dioxide and water; (4) *hydrogen selenate* (H_2SeO_4), a solid melting at 58° whose aqueous solution (selenic acid) resembles sulfuric acid in properties and chemical conduct; (5) salts derived from the acids H_2Se , H_2SeO_3 , and H_2SeO_4 , which in a general way resemble those of the corresponding sulfur compounds. Selenium oxychloride, a liquid of the composition indicated by the formula SeOCl_2 , is an excellent solvent for a wide range of materials.

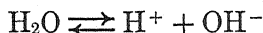
Tellurium. While small quantities of tellurium occur in nature in the free state, it is much more frequently found combined with metals, especially gold, silver, lead, and bismuth, forming compounds known as *tellurides*. In separating these metals from their ores, considerable quantities of tellurium are often obtained, although no important commercial use has as yet been found for it. The pure element resembles the metals in appearance. It has a silvery luster, and, like the metals, it conducts electricity. When heated in the air, it burns, forming tellurium dioxide (TeO_2).

Compounds of tellurium. Some of the more important compounds of tellurium are the following: (1) *hydrogen telluride* (H_2Te), a gas of most disagreeable odor, which resembles hydrogen sulfide in its properties; (2) *tellurium dioxide* (TeO_2), a white solid formed by the combustion of tellurium in oxygen or in air; (3) *tellurium trioxide* (TeO_3), an orange-yellow solid formed by the careful heating of hydrogen tellurate; (4) *hy-*

drogen tellurite (H_2TeO_3), a white powder formed by the oxidation of tellurium with nitric acid; (5) *hydrogen tellurate* (H_2TeO_4), a solid formed by the action of strong oxidizing agents upon tellurium, whose aqueous solution (telluric acid) has very weak acid properties. Salts of the different acids of tellurium are also known.

HYDROLYSIS

While for most purposes we make no important error in assuming that water is a nonionized compound, there are many reactions that keep reminding us that even the purest of water has a *slight* but measurable degree of ionization. The gram-molar concentration of the H^+ and the OH^- ions in pure water is 1×10^{-7} at 21° (p. 341), which corresponds to about 0.1 mg of H^+ and 1.7 mg of OH^- per ton. While this is very small expressed in *weight*, it still means millions of each kind of ions per cubic centimeter, and also that *these are constantly maintained* through the equilibrium

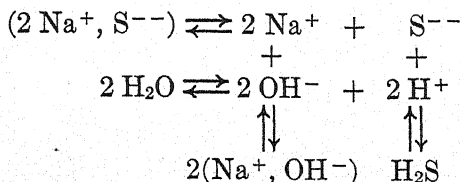


Because of this distinct (though slight) ionization, water takes part in many reactions of the type we have been calling double decomposition, all of which depend upon the presence of free ions in solution. A reaction of double decomposition that depends upon the presence of the ions formed from water is called *hydrolysis*. The process of hydrolysis is just the reverse of that of neutralization.

Under certain conditions some salts show a very marked degree of hydrolysis in solution, and the salts of the various acids of sulfur illustrate the principles involved very admirably. We may therefore with profit study the subject of hydrolysis of salts at this point.

Hydrolysis of salts. The hydrolyzing action of water with salts presents four distinct cases, which will be considered in order.

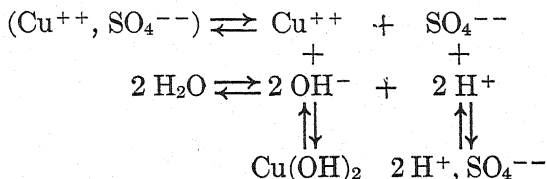
1. *Hydrolysis of a salt derived from a strong base and a weak acid.* All salts derived from a strong base and a weak acid have an *alkaline* reaction in solution, and consequently there must be an excess of hydroxyl ions in the solution. Sodium sulfide, derived from sodium hydroxide and hydrosulfuric acid, will serve as an example. If this salt is added to water, the following reactions take place:



In one of these the product formed, H_2S , is a *very weak acid* (little ionized), and equilibrium is not reached until almost all the hydrogen ions have entered into combination. In the other equilibrium the product formed, NaOH , is a *strong base* and is largely ionized. As a result of these differences more hydrogen ions are withdrawn in one equilibrium than hydroxyl ions in the other, and the solution *acquires basic properties from the excess of hydroxyl ions*.

2. Hydrolysis of a salt derived from a strong acid and a weak base.

Salts belonging to this class yield *acid* solutions, and consequently these solutions must have an excess of hydrogen ions. Copper sulfate will serve as an example. When this salt is dissolved in water, the equilibria represented in the following equations result:

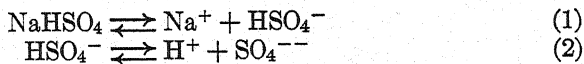


In one of these the product formed, $\text{Cu}(\text{OH})_2$, is a *very weak base* (little ionized), and at equilibrium most of the hydroxyl ions are withdrawn from the solution. With sulfuric acid formed in the other equilibrium the case is different because it is a *strong acid* and is largely ionized. As a result of these differences more hydroxyl ions are withdrawn than hydrogen ions, and consequently the *solution acquires acid properties*.

3. Hydrolysis of a salt derived from a strong base and a strong acid. All such salts yield neutral, or nearly neutral, solutions. It is evident from the above discussions that when salts of this class are dissolved in water, neither the hydrogen nor the hydroxyl ions are withdrawn in appreciable amounts; hence their solutions are approximately neutral.

4. Hydrolysis of a salt derived from a weak base and a weak acid. Such salts are more or less completely hydrolyzed in the presence of water, especially if one of the products formed is insoluble.

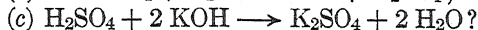
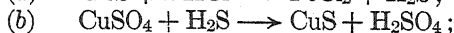
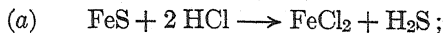
The action of water upon acid salts. The acid salts of *strong* acids readily ionize in aqueous solutions, yielding hydrogen ions. Thus sodium hydrogen sulfate ionizes as follows:



In dilute solutions both of the reactions expressed in (1) and (2) are practically complete. Such solutions, therefore, have an acid reaction due to the

6. What property does sulfuric acid possess that makes the acid applicable to the preparation of many other acids?

7. Why do the following reactions go to completion:



8. Why does an aqueous solution of sodium carbonate react basic toward litmus, while a similar solution of sodium sulfate reacts neutral or nearly so?

9. How do you account for the fact that aluminum sulfide is completely decomposed by water?

10. Which solution would have the greater $[\text{S}^{--}]$: (a) water saturated with H_2S ; (b) a 1 *N* HCl solution saturated with H_2S ?

Problems

1. Ten cubic centimeters of a normal solution of sulfuric acid was added to 15 cc of a normal solution of sodium hydroxide, and the resulting solution evaporated to dryness and heated so as to expel all water present. (a) What is the composition of the residue? (b) Calculate its weight.

2. (a) What weight of iron sulfide is necessary for preparing sufficient hydrogen sulfide to precipitate the copper present in an aqueous solution of 50 g of copper sulfate (assume that all the hydrogen sulfide is utilized)? (b) Calculate the weight of the copper sulfide precipitated.

3. A compound was analyzed and found to have the following percentage composition: oxygen, 25.69; sulfur, 13.00; magnesium, 9.86; water of hydration, 51.16. (a) Calculate its formula. (b) What is the name of the compound?

4. Calculate from the following data the percentage of hydrogen sulfate in a sample of sulfuric acid: 10 g of the sulfuric acid was dissolved in 100 cc of water and neutralized with a normal solution of sodium hydroxide; 50 cc of the sodium hydroxide solution was required to effect neutralization.

5. If 95 per cent of the sulfur is utilized, what is the daily consumption of sulfur in an industrial plant whose daily output is 100 tons of sulfuric acid containing 98.5 per cent of hydrogen sulfate?

6. (a) One hundred liters of hydrogen sulfide will require how many liters of oxygen for complete combustion? (b) How many liters of sulfur dioxide will be formed (all gases measured under the same conditions)?

Reading References

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- CHANDLER and FRASCH. The award of the Perkin Medal to Frasch and the address of acceptance, *Industrial and Engineering Chemistry*, Vol. IV, pp. 132-140. The medal was awarded to Frasch for his development of a method for mining sulfur.
- CLARKE. *Marvels of Modern Chemistry*. Chapter XIV tells of sulfur.
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- CUNNINGHAM. "Sulfur," a series of three articles in the *Journal of Chemical Education*, Vol. XII, pp. 17-23, 83-87, and 120-124. Interesting and well illustrated.
- FOSTER. *Romance of Chemistry*. Chapter XII is entitled "Sulfur, A Pillar of Industry."
- MASON. "The Sulfur Industry, History and Development," *Industrial and Engineering Chemistry*, Vol. XXX, pp. 740-746.
- SPANGLER. "Recent Developments in the Manufacture of Sulfuric Acid," *Industrial and Engineering Chemistry*, Vol. XXI, pp. 417-421.
- WEEKS. *The Discovery of the Elements*. The story of the discovery of sulfur, selenium, and tellurium, interestingly told. See index for pages.
- Consult the Minerals Yearbook for facts concerning the production of sulfuric acid.

Compounds of Nitrogen

Introduction. In Chapter 9 the properties of the element nitrogen, a constituent of the atmosphere, were described. We shall now consider some of the chief compounds of this important and interesting element (Fig. 226).

The unstable character of compounds of nitrogen. Experiment shows that the molecule of nitrogen has the formula N_2 , and that these molecules are very inactive at ordinary temperatures. A great deal of energy is required to decompose them into atoms, into which they must be converted before entering into combination with other elements. On the other hand, many compounds of nitrogen are unstable; and the nitrogen atoms tend to leave such compounds to form stable nitrogen molecules. It is partly due to this fact that certain nitrogen compounds, such as nitrocellulose and nitroglycerin, are so extensively used as constituents of explosives.

While many thousands of compounds of nitrogen are known, we can study only some of the more simple ones, namely, those which nitrogen forms with hydrogen or oxygen or with both.

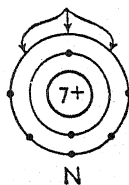


FIG. 226. Diagram of Nitrogen Atom. (Arrows indicate unfilled positions).

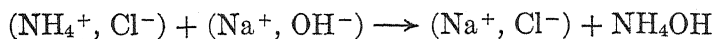
COMPOUNDS OF NITROGEN WITH HYDROGEN

Nitrogen forms three important compounds with hydrogen, the names and formulas of which are as follows: *ammonia* (NH_3), a gas, and *hydrazine* (N_2H_4) and *hydrazoic acid* (HN_3), both liquids.

Ammonia (NH_3). Since ammonia is formed in certain natural processes which are constantly taking place about us, such as the decay of nitrogenous organic matter, it is easy to understand why this compound has been known for so long a time. It was originally prepared by heating the hoofs and horns of animals, and the aqueous solution of the gas so obtained was termed *spirits of hartshorn*. The pure gas itself was first prepared by Priestley in 1774, and its composition was determined soon after by the French chemist Berthollet.

Preparation of ammonia. Ammonia can be prepared in a number of ways, the most important of which are the following :

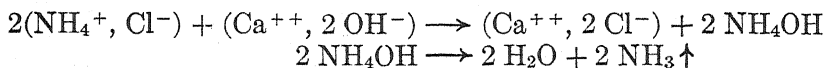
1. **Laboratory method.** Ammonia is usually prepared from ammonium chloride (NH_4Cl), a colorless salt often obtained in the manufacture of coal gas. When a mixture of ammonium chloride and sodium hydroxide is heated in the presence of a small quantity of water, the ammonium ion and sodium ion change places, as indicated in the following equation :



The resulting ammonium hydroxide (NH_4OH) is unstable and, as fast as it is formed, breaks down into water and ammonia :



Calcium hydroxide, $\text{Ca}(\text{OH})_2$, is frequently used in place of the more expensive sodium hydroxide :



Experimental details. The mixture of ammonium chloride and calcium hydroxide is introduced into a flask A with a little water (Fig. 227) and gently heated. Ammonia is evolved and may be collected by bringing the end of the exit tube inside and near the bottom of an inverted bottle B, as shown in the figure. The gas, which is lighter than air, collects in the bottle, gradually forcing the air out at the mouth.

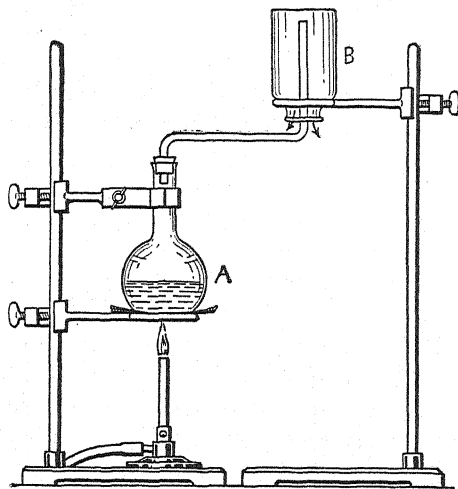


FIG. 227. Diagram of Apparatus Used in Laboratory Preparation of Ammonia

2. **Methods used in industry.** (a) *From coal.* Until comparatively recent years nearly all the ammonia used commercially in the United States was obtained as a by-product in the manufacture of coal gas and coke. Certain grades of soft coal contain, in addition to carbon, about

1 per cent of nitrogen and 7 per cent of hydrogen, as well as small percentages of other elements. When this coal is heated in retorts

from which the air is excluded, not only are the combustible gases which constitute coal gas formed, but also ammonia and many other valuable products. From 25 to 50 per cent of the nitrogen in the coal is converted into ammonia, and much of the remainder is set free as molecular nitrogen. The gases expelled from the coal are passed through water, which absorbs the ammonia, together with certain other compounds, forming a solution known as the *ammoniacal liquor*. When this liquor is heated with slaked lime (Ca^{++} , 2OH^-), ammonia is evolved and is absorbed either in water or in a dilute acid solution.

(b) *By the direct combination of nitrogen and hydrogen (the Haber process)*. When nitrogen and hydrogen are mixed together in the proportion in which they are combined in ammonia, and the mixture is heated, a small percentage of ammonia is formed, in accordance with the following equation :



The low yield is due to the fact that under ordinary conditions the equilibrium expressed in the equation given above is reached when about 2 per cent of ammonia has been formed. The German chemist Haber and his co-workers discovered that this yield could be greatly increased by modifying the conditions of temperature and pressure under which the reaction is carried out and by using a suitable catalyst. The Haber process was developed in Germany under stress of wartime conditions, when the natural sources of nitrogen compounds (chiefly Chilean saltpeter, NaNO_3) were cut off. This process, or some modification of it, is now the principal one used for the manufacture of ammonia on a large scale (Fig. 228).

The conditions for a maximum yield are high pressure and a comparatively low temperature. Thus, the experiments carried on in the Fixed Nitrogen Research Laboratory, maintained by the Federal government at Washington, D.C., show that a yield of 98.29 per cent of ammonia is obtained when the mixture of gases is heated to a temperature of 200° under a pressure of 1000 atm. A great many catalysts have been used; one of the most effective consists of finely divided iron mixed with a small percentage of potassium aluminate.

Properties. Ammonia is a colorless gas having a strong, suffocating odor. Under standard conditions 1 l of the pure gas weighs 0.7708 g (0.59 times as heavy as air). Its critical temperature is 132.4° , at which temperature it is liquefied by a pressure of 111.5 atm. Liquid ammonia is colorless and boils at -33.3° . Its properties have

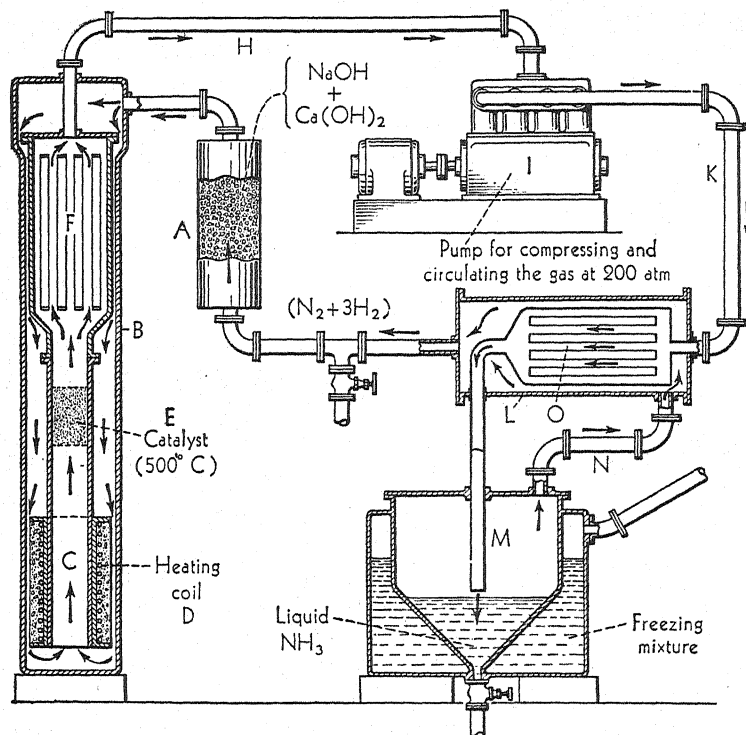


FIG. 228. Diagram Illustrating the Principle of the Haber Process

The mixture of nitrogen and hydrogen is dried by passing it through container A. The dried gases then pass on, as indicated by the arrows, down to the bottom of container B, through the heating coil D, up tube C, and then through the catalyst E, where the combination of the two gases takes place. The resulting mixture of ammonia, nitrogen, and hydrogen passes upward through the tubes F and is somewhat cooled by the current of nitrogen and hydrogen which passes down the container B. The mixture flows on through H and down into the container L, where it is still further cooled by passing over the tubes O. It then passes into the vessel M, which is kept cooled by a freezing mixture. Here the ammonia separates in liquid form, while the uncombined nitrogen and hydrogen pass upward through N into the outer jacket of L and back again into the drying tube A. Additional quantities of nitrogen and hydrogen are constantly added to take the place of those withdrawn in the formation of ammonia.

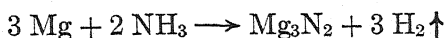
been extensively studied by the American chemist E. C. Franklin, who has shown that, like water, it is not only an excellent solvent but also a highly ionizing one. At low temperatures ammonia can be obtained in the form of a snowlike solid which melts at -77.7° .

A noteworthy property of ammonia is its extreme solubility in water. This solution is called *aqua ammonia*. Under a pressure of 1 atm 1 l of water dissolves 1298.9 l of the gas at 0° , and 710 l at 20° .

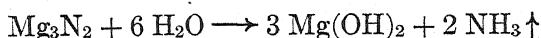
On account of the expansion of the liquid the resulting solutions have a density less than that of water, as is shown in the following table :

Density	1.00	0.995	0.990	0.980	0.970	0.950	0.930	0.910	0.890	0.880
Per cent by weight of NH ₃	0.00	1.14	2.31	4.80	7.31	12.74	18.64	24.99	31.73	35.60

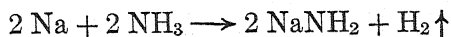
Chemical conduct. Since ammonia is decomposed when heated, liberating free hydrogen, it acts as a reducing agent and reduces certain metallic oxides to the free metal. The hydrogen in the compound readily burns in an atmosphere of pure oxygen, liberating the nitrogen ; but combustion will not take place in air unless heat is continuously applied from an external source. Certain metals, such as magnesium and lithium, react with ammonia to liberate all the hydrogen present and form *nitrides* :



These nitrides are solids and react with water to form ammonia :



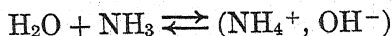
Sodium and potassium, on the other hand, liberate only a part of the hydrogen :



The group NH₂ is termed the *amido* (or *amino*) group, and the compound NaNH₂ is called *sodium amide*, or *sodamide*. It is a white solid and has important commercial uses.

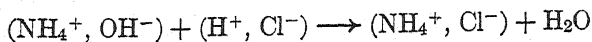
Like water, ammonia combines directly with certain salts to form *ammoniates*, analogous to hydrates. Thus, with calcium chloride it forms the ammoniate CaCl₂ · 8 NH₃.

Action of ammonia with water. A solution of ammonia in water is basic in character. This property is accounted for by the fact that to some extent hydrogen ions (H⁺) leave water molecules to unite with ammonia molecules :



When heated, aqua ammonia acts as if it were solely a solution of ammonia in water ; for as fast as the ammonia is driven out by heat, the equilibrium existing between the ions represented in the equation is shifted, with the result that more ammonia is formed. If the heating is continued, therefore, all the ammonia is finally driven out. On the other hand, when treated with an acid, aqua ammonia acts as if it were a solution containing hydroxyl ions (OH⁻) ; for as fast as these are neutralized by the acid, more are formed as long as any free ammonia remains in solution. Thus, when

hydrochloric acid is added to aqua ammonia, ammonium chloride and water are formed :

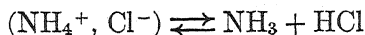


When the water is evaporated, the ammonium chloride is left in the form of a colorless solid. Similarly, nitric and sulfuric acids form, respectively, ammonium nitrate, NH_4NO_3 , and ammonium sulfate, $(\text{NH}_4)_2\text{SO}_4$.

Ammonium salts. The salts of the univalent ammonium ion, NH_4^+ , closely resemble the corresponding salts of the sodium ion in their formulas and chemical properties. Practically all ammonium salts are soluble, which enhances their value as chemical reagents. Small quantities of ammonium salts are found in the soil and in sea water. All the common ammonium salts are colorless solids and may be obtained not only by neutralizing ammonium hydroxide solutions but also by the direct combination of ammonia with the anhydrous acids :



When heated, ammonium chloride volatilizes, but is dissociated into ammonia and an acid in a reversible reaction :



A number of other ammonium salts act in this same way, although some are permanently decomposed by heating.

Ammonium chloride, NH_4Cl , is used in medicine and in making dry cells. It is also used as a flux in soldering and as a chemical reagent. Ammonium bromide and iodide, which are used in photography, closely resemble the chloride, although the iodide readily absorbs moisture upon exposure to air and decomposes to such an extent that the free iodine liberated colors the salt. The fluoride, NH_4F , attacks silicates and is used for etching glass. Ammonium sulfate, $(\text{NH}_4)_2\text{SO}_4$, and the ammonium phosphates, $(\text{NH}_4)_2\text{HPO}_4$ and $(\text{NH}_4)_3\text{PO}_4$, are important fertilizers, while ammonium nitrate, NH_4NO_3 , is a constituent of certain explosives (*ammonal*). Ammonium sulfide, $(\text{NH}_4)_2\text{S}$, and carbonate, $(\text{NH}_4)_2\text{CO}_3$, are important laboratory reagents. Since these two compounds are salts of weak acids with a weak base, they are extensively hydrolyzed. The carbonates of ammonia are used as smelling salts.

Composition of ammonia. That ammonia is a compound of nitrogen and hydrogen is proved by the fact that it may be formed by the direct union of the two elements. The quantitative composition of the compound may be determined by taking advantage of

certain reactions which make it possible to liberate the nitrogen as well as the hydrogen from any definite volume of ammonia. By

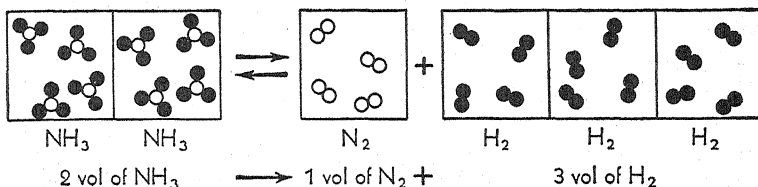


FIG. 229. *Volume Relations between Ammonia and the Nitrogen and Hydrogen Which Combine to Form It*

measuring the volumes of the gases so liberated one can compare them not only with each other but also with the volume of the ammonia from which they were derived. In this way it has been proved that on decomposition 2 volumes of ammonia yield 1 volume of nitrogen and 3 volumes of hydrogen, as expressed graphically in Fig. 229. Of course the reverse is likewise true: 3 volumes of hydrogen combine with 1 volume of nitrogen to form 2 volumes of ammonia. It will be observed that these volume relations are in accord with Gay-Lussac's law of combining volumes.

Uses of ammonia. Large quantities of ammonia are used in the manufacture of nitric acid and of aqua ammonia, as well as in the preparation of ammonium sulfate, widely used as a constituent of fertilizers. In the liquid state it is also used extensively as a refrigerating liquid in the manufacture of artificial ice (Fig. 230).

Hydrazine (N_2H_4). This compound may be regarded as having the formula $\text{NH}_2\text{--NH}_2$. It is composed of two amido groups, just as hydrogen peroxide is composed of two hydroxyl groups (HO--OH). It is a colorless liquid boiling at 113.5° . Like ammonia, it combines with water to form a base from which salts can be prepared by the action of acids. For example, with hydrochloric acid it forms hydrazine hydrochloride, a colorless solid having the formula ($\text{NH}_2\text{--NH}_3^+, \text{Cl}^-$).

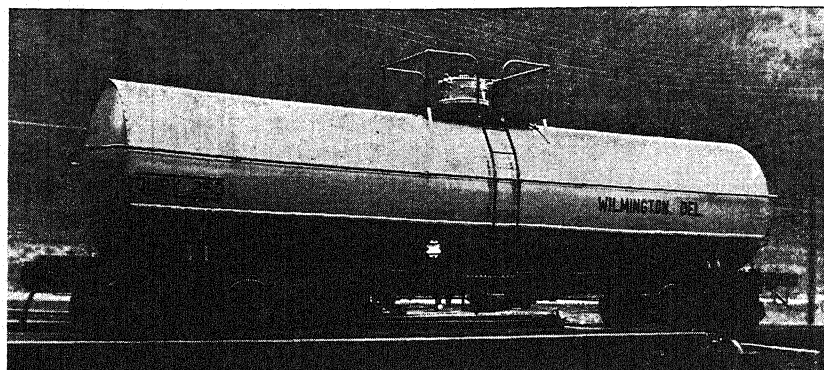
Hydrazoic acid (HN_3). This acid is a colorless liquid of disagreeable odor. It boils at 37° , and the acid, as well as most of its salts, is violently explosive.

COMPOUNDS OF NITROGEN WITH HYDROGEN AND OXYGEN

The most important of these compounds are the following:

Hyponitrous acid ($\text{H}_2\text{N}_2\text{O}_2$), a colorless, unstable solid.

Nitrous acid (HNO_2), known only in dilute solution.



E. I. du Pont de Nemours & Co.

FIG. 230. A Tank Car of Liquid Ammonia

Nitric acid (HNO_3), a colorless liquid.

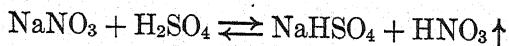
Hydroxylamine (NH_2OH), a white crystalline solid.

The solutions of the first three of these compounds are acids, as is indicated by the names; the solution of the last is a base. Nitric acid will be described first, since it is by far the most important compound of the group.

Nitric acid. Nitric acid was well known to the alchemists. In the ninth century the alchemist Geber prepared it from saltpeter (KNO_3) by a process somewhat similar to that used in the laboratory at the present time, and the Germans still call it *Salpetersäure*.

Preparation of nitric acid. In nature every flash of lightning is attended by the formation of some nitric acid. The electric sparks cause the nitrogen and oxygen of the air to combine to form oxides of nitrogen, which then react with atmospheric moisture to form nitric acid. In 1903 two Norwegians, Birkeland and Eyde, successfully developed this reaction into a commercial process for making nitrates, but the method has been almost entirely abandoned because of the excessive cost of electric power. Two important methods for preparing nitric acid are the following:

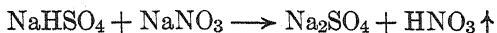
1. **Laboratory method.** Nitric acid is prepared in the laboratory by the action of sulfuric acid upon sodium nitrate, as indicated in the following equation:



The reaction is a reversible one, and at ordinary temperatures equilibrium soon results. If, however, a gentle heat is applied to the mixture, the nitric acid is removed as fast as formed, since it has a relatively low boiling point (86°), and may be recovered by

condensing the vapors (Fig. 231). Under these conditions the reverse reaction cannot take place, and the action between the sodium nitrate and the sulfuric acid continues until it is completed.

If double the weight of sodium nitrate indicated in the equation is used, and the mixture is heated to a higher temperature, the sodium hydrogen sulfate which is first formed reacts with the excess of sodium nitrate to form the normal sodium sulfate and nitric acid:



This additional amount of nitric acid is formed without using any additional sulfuric acid. The higher temperature required to bring about the reaction, however, partly decomposes the nitric acid, so that the reaction is not an economical one.

2. Commercial method; preparation from ammonia. Inasmuch as the natural supplies of nitrates are limited, many experiments have been carried out in the hope of finding some method of preparing the acid and its salts (the nitrates) from the inexhaustible supplies of nitrogen and oxygen in the air. These experiments have been successful, and the method developed has replaced the older methods entirely. In the new method ammonia is first produced by the Haber process (p. 379) and then oxidized by the oxygen in the air. This last step, which results in the formation of nitric acid, is accomplished by passing a mixture of ammonia and air through tubes or chambers containing a suitable catalyst (Fig. 232). Many experiments have been carried out in order to find the most effective catalyst. Hot platinum gauze seems to be the best, although the much cheaper iron oxide has also been used.

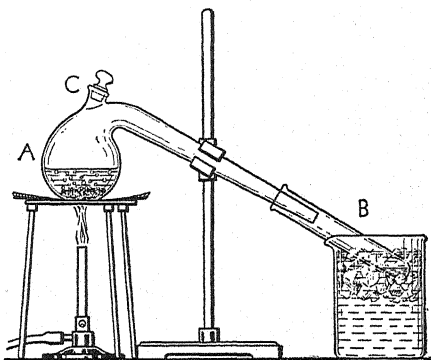
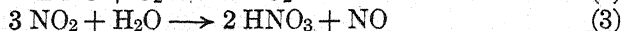
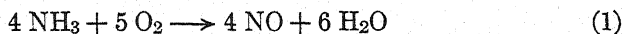


FIG. 231. *Laboratory Preparation of Nitric Acid*

Sodium nitrate is introduced into a retort A and sulfuric acid added. If the retort is gently heated, the nitric acid distills over as fast as formed, and is condensed in a tube B kept cool by ice water.

The reactions involved in the process vary somewhat with conditions, but in a general way they may be expressed by the following equations:



The nitric oxide (NO) generated according to equation (3) is again oxidized to nitrogen dioxide (NO₂), as indicated in equation (2). When carried out under atmospheric pressure, the nitric acid formed contains about 60 per cent of HNO₃. This acid can be further concentrated, if

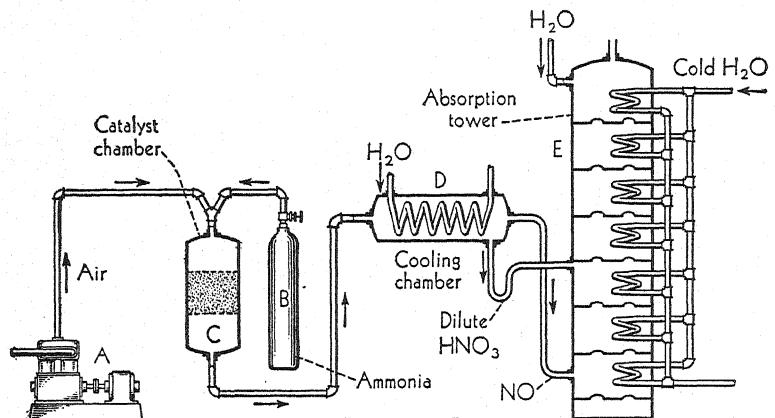
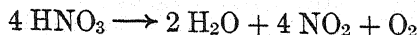


FIG. 232. *Diagram of Essential Parts of Apparatus Used for Preparing Nitric Acid on a Large Scale by Oxidation of Ammonia*

Filtered air, which furnishes the oxygen required for the oxidation of the ammonia, is forced by the pump A into the catalyst chamber C. As it enters the chamber, it meets a stream of gaseous ammonia supplied from the container B. The mixture of the two gases, air and ammonia, then passes over the catalyst contained in C, where oxidation of the ammonia takes place. The hot oxidation products resulting are cooled somewhat by passing them through a chamber (not shown in the figure) through which the air is passed in pipes before it enters the catalyst chamber. This serves the double purpose of pre-heating the air used and of cooling the oxidation products. The oxidation products then pass through the cooling chamber D. Here a small percentage of nitric acid is formed by the interaction of the products of oxidation. Both the dilute nitric acid and the nitric oxide then enter the absorption tower, where the reaction continues, forming nitric acid containing about 60 per cent HNO₃. This can be further concentrated, if desired

desired, by adding sulfuric acid and distilling the mixture. This method, first devised in Germany, has been greatly improved in the United States, so that now all the nitric acid used for commercial purposes is prepared in this way.

Preparation of pure nitric acid (hydrogen nitrate). Pure nitric acid (more properly called *hydrogen nitrate*, to distinguish it from its aqueous solutions) readily decomposes into water, nitrogen dioxide, and oxygen, as represented in the following equation :



The nitrogen dioxide resulting from the decomposition is a reddish-brown gas which dissolves in the liquid, giving it a yellowish color. Because of its unstable character, hydrogen nitrate is difficult to prepare. By heating sulfuric acid and sodium nitrate in a retort under diminished pressure, pure hydrogen nitrate is obtained as a distillate.

Properties. Pure hydrogen nitrate is a colorless liquid which has a density of 1.502 and boils at 86° with partial decomposition. At -42° it freezes to a snowlike solid. An aqueous solution containing 68 per cent of hydrogen nitrate has a constant boiling point of 120.5° under a pressure of 735 mm and distills with unchanged concentration. This solution has a density of 1.4 and constitutes the *concentrated nitric acid* of commerce.

Chemical conduct. Nitric acid is one of the strongest of acids, forming the ions H^{+} and NO_3^{-} in aqueous solutions. Because of its unstable character and large percentage of oxygen, concentrated nitric acid acts as a strong oxidizing agent. For example, it oxidizes charcoal to carbon dioxide, and sulfur to sulfuric acid.

Nitric acid readily reacts with many organic compounds, sometimes with explosive violence. Under carefully regulated conditions it forms compounds of the greatest commercial importance. Thus, with glycerin it forms *nitroglycerin*, which is the principal active constituent of dynamite; likewise with cellulose, the chief constituent of wood and cotton, it forms *nitrocellulose*, whose many commercial uses will be described in a later chapter.

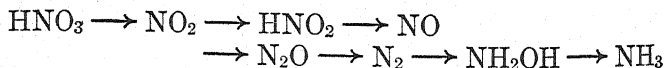
Action of nitric acid on metals. All the metals, with the exception of gold, platinum, and a few of the rare metals, are acted upon more or less readily by nitric acid. In discussing the action of nitric acid upon these metals it is convenient to divide them into two classes:

1. *Metals occurring above hydrogen in the electromotive series.*

At first thought it might be expected that hydrogen would be evolved when a dilute solution of nitric acid is acted upon by any of the metals occurring above hydrogen in the electromotive series of metals (p. 277); and indeed it is evolved to a certain extent with a few of the metals, such as magnesium.

When one recalls, however, that nitric acid is a strong *oxidizing* agent, while hydrogen has strong *reducing* properties, it seems reasonable to suppose that nitric acid would be reduced by any hydrogen set free, yielding reduction products. Experiments show that this is what actually happens. The particular reduction products formed in any case depend upon the metal, the concentration of the acid, the temperature, and other conditions under which the

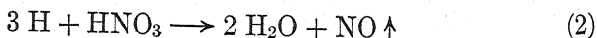
reaction takes place. The following compounds represent successive steps in the reduction of nitric acid :



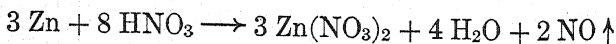
It is possible, by selecting different metals and by modifying the conditions of the reaction, to obtain any of these products. *Under ordinary conditions, however, nitric oxide (NO) is the principal compound formed.* The course of the reaction may be shown by the study of a typical example, such as the action of nitric acid of medium concentration upon zinc. The first step in the reaction consists in the formation of zinc nitrate and hydrogen :



The hydrogen is not evolved as molecules (H_2) but as *nascent* atoms, and they at once react with the nitric acid :

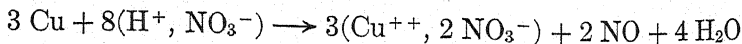


The products of the reaction between zinc and the acid, therefore, are zinc nitrate, water, and nitric oxide, as represented in the following equation, obtained by multiplying equation (1) by 3 and equation (2) by 2, and adding the two equations :

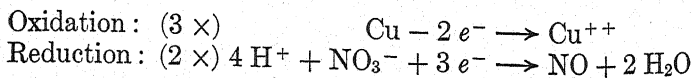


2. Metals occurring below hydrogen in the electromotive series.

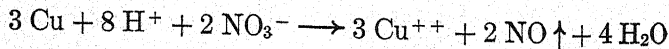
Those metals that occur below hydrogen in the electromotive series, when acted upon by nitric acid, yield the same products as the metals above hydrogen in the series, but probably by a different mechanism. The general equation representing the reaction with copper is the same as that representing the reaction with zinc :



To show the steps in the reaction, the equation may be broken down into two ion-electron equations :



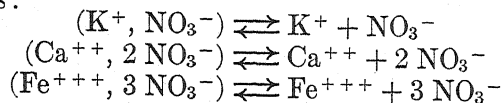
Since two electrons are lost in the first equation and three gained in the second, it is necessary to multiply the first by 3 and the second by 2 before adding to obtain the ionic equation



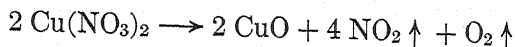
The final, complete reaction would then be



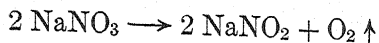
Salts of nitric acid — the nitrates. The salts of nitric acid are called *nitrates*. They can be obtained by the general method used for preparing salts, such as the action of nitric acid upon the metals themselves or upon their oxides or hydroxides. Some of these, especially sodium nitrate and potassium nitrate, are found in nature. The nitrates of most of the metals are white crystalline solids. The nitrate of copper is blue, that of nickel is green, while cobalt nitrate is cherry red. All the normal nitrates are soluble in water and furnish the ions M^+ and NO_3^- , in which M represents the metal. Thus, potassium, calcium, and iron nitrates, already ionized in their crystals, yield their ions to the solution, as represented by the following equations:



When heated, the nitrates undergo decomposition. As a rule the metal is left in the form of its oxide, while oxygen and oxides of nitrogen are evolved. Thus, when copper nitrate is heated, the blue color of the nitrate gradually gives way to the black color of copper oxide, while the evolution of nitrogen dioxide is indicated by the reddish color of the evolved gas:

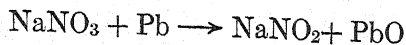


In the case of a few nitrates, however, oxygen alone is evolved. Thus, sodium nitrate, when heated, forms sodium nitrite (NaNO_2) and oxygen:



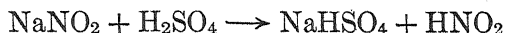
The nitrates have various uses. Large quantities of sodium nitrate are exported from Chile to different countries, where it is used for the most part in fertilizers.

Nitrous acid (HNO_2). Sodium nitrite (NaNO_2), the sodium salt of nitrous acid, is readily formed by heating sodium nitrate with a mild reducing agent such as lead:

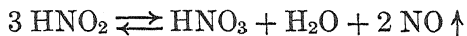


When this nitrite is treated with sulfuric acid, we should expect to have nitrous acid liberated (just as nitric acid is formed from

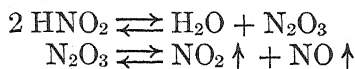
a nitrate under similar conditions), according to the following equation:



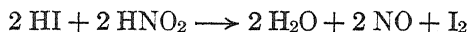
If this reaction is carried out in very dilute solution, some nitrous acid is obtained; but the acid is so unstable that it soon decomposes, thus:



In solutions at all concentrated the acid decomposes as fast as generated, forming water and oxides of nitrogen, as follows:



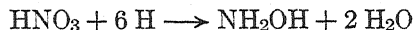
Nitrous acid may act as either an oxidizing agent or a reducing agent, depending on conditions. Thus, hydrogen iodide (a compound easily decomposed into hydrogen and iodine) is oxidized by the nitrous acid, as shown in the following equation:



On the other hand, in the presence of a compound that readily gives up oxygen, nitrous acid combines with this oxygen, being changed thereby to nitric acid.

Hyponitrous acid ($\text{H}_2\text{N}_2\text{O}_2$). When sodium nitrate is reduced under carefully regulated conditions, there is formed a compound, $\text{Na}_2\text{N}_2\text{O}_2$, called sodium hyponitrite. This is the sodium salt of *hyponitrous acid* ($\text{H}_2\text{N}_2\text{O}_2$). The free acid can be obtained from this salt in the form of colorless crystals, but it is very unstable and even likely to explode.

Hydroxylamine (NH_2OH). This compound may be regarded as being composed of a hydroxyl group and an amino group, thus: $\text{NH}_2\text{—OH}$. It is intermediate between hydrogen peroxide (HO—OH) and hydrazine ($\text{NH}_2\text{—NH}_2$). Hydroxylamine was first obtained in dilute solution in 1865; but the compound was not isolated in a pure state until 1891, when De Bruyn obtained it in the form of colorless needles melting at 34° . It is formed by the action of nascent hydrogen on nitric acid:



It is often formed, therefore, when certain metals are dissolved in nitric acid.

Hydroxylamine resembles ammonia in being soluble in water and combining with it to form a base, (NH_3OH^+ , OH^-). This base, however, is much less ionized and therefore weaker than ammonium hydroxide. By the action of strong acids the corresponding salts may be obtained. Thus,

with hydrochloric acid there is formed the chloride (NH_3OH^+ , Cl^-). These salts are more stable than the free compound and are therefore more largely used.

COMPOUNDS OF NITROGEN WITH OXYGEN

The names, formulas, and physical state of the oxides of nitrogen are as follows:

Nitrous oxide (hyponitrous anhydride) (N_2O), a colorless gas.

Nitric oxide (NO), a colorless gas.

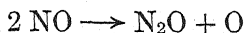
Nitrogen dioxide (NO_2), a gas, deep reddish brown in color.

Nitrogen trioxide (nitrous anhydride) (N_2O_3) exists only at low temperatures, both in liquid and in solid form.

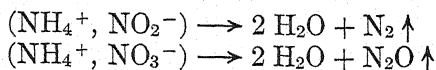
Nitrogen pentoxide (nitric anhydride) (N_2O_5), a white crystalline solid.

Nitrous oxide (laughing gas) (N_2O). Nitrous oxide was first prepared by Priestley in 1772, two years previous to his discovery of oxygen. Davy determined its composition in 1800 and was the first to point out its physiological properties.

Preparation. Nitrous oxide can be prepared by the action of suitable reducing agents upon nitric acid as well as upon nitric oxide. Priestley first obtained it from nitric oxide by the reducing action of iron:



It is most conveniently prepared by heating ammonium nitrate. Just as ammonium nitrite, when heated, yields water and nitrogen (p. 147), so ammonium nitrate decomposes in a similar way, forming water and nitrous oxide. The similarity between the two reactions is shown in the following equations:



Properties. Nitrous oxide is a colorless gas 1.53 times as heavy as air. It has a faint odor and its solution has a slightly sweetish taste. Liquid nitrous oxide is colorless and boils at -89.5° .

Chemically nitrous oxide is characterized by the ease with which it decomposes into free nitrogen and oxygen. It is therefore a good oxidizing agent. Such substances as carbon, iron, and phosphorus, when ignited and placed in jars of the gas, burn with brilliancy, forming oxides and nitrogen. When inhaled it produces a kind of hysteria (whence the name *laughing gas*) and even unconsciousness and insensibility to pain. Davy (Fig. 190), who discovered this

property of the gas, states that after breathing it he "danced about the laboratory as a madman." It has long been used as an anesthetic for minor surgical operations, such as those of dentistry, and is sold for this purpose, condensed in suitable containers.

Nitric oxide (NO). This gas was known as early as 1600. It is formed when electric sparks are passed through a mixture of oxygen and nitrogen, but in the laboratory it is most readily prepared by the action of nitric acid (density, 1.2) upon certain metals, such as copper (p. 388).

Laboratory preparation. The metal is placed in a flask *A* (Fig. 233), and the acid slowly added through the funnel tube *B*. The gas escapes through *C* and is collected over water. The gas at first evolved combines with the oxygen of the air contained in the flask to form the reddish-brown nitrogen dioxide, but this is absorbed as it bubbles through the water.

Properties. Nitric oxide is a colorless gas slightly heavier than air. It can be condensed to a liquid which boils at -151° . Nitric oxide is a much more stable compound than nitrous oxide; nevertheless it can be decomposed into its elements without difficulty. If a bit of phosphorus is barely ignited and at once introduced into a jar of the gas, the flame is extinguished. On the other hand, if the phosphorus is first heated until vigorous combustion begins, and is then introduced into the gas, the combustion continues with great brilliancy. One of the most characteristic properties of nitric oxide is its conduct toward oxygen. When brought in contact with oxygen (or air), it forms nitrogen dioxide (NO_2).

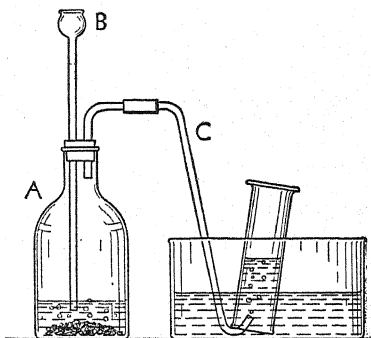
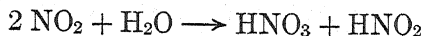


FIG. 233. *Laboratory Preparation of Nitric Oxide*

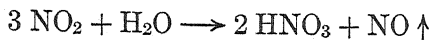
Nitrogen dioxide (NO_2). Nitrogen dioxide may be obtained by heating the nitrates of many of the heavier metals, such as lead nitrate or copper nitrate, or by the direct union of nitric oxide and oxygen (Fig. 234). At ordinary temperatures it is a reddish-brown gas. When the gas is cooled the color fades, and a light-yellow liquid is obtained which boils at 21.3° and freezes to an almost colorless solid at -9.3° .

Nitrogen dioxide gives up half of its oxygen very easily, being converted into nitric oxide, and is a good oxidizing agent. It acts

upon water in either of two ways, depending upon the temperature. In cold water both nitric and nitrous acids are formed :



At higher temperatures the nitrous acid decomposes as fast as formed, and the reaction may be represented as follows :



Preparation of nitrogen dioxide. The formation of nitrogen dioxide from nitric oxide and oxygen, together with the reaction between the dioxide

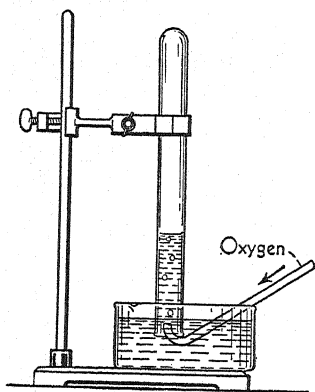
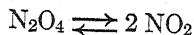


FIG. 234. The Formation of Nitrogen Dioxide

and water, may be shown as follows : A tube is filled with water and inverted in a vessel of water, as shown in Fig. 234. The tube is then nearly filled with nitric oxide, after which oxygen is admitted, a few bubbles at a time. As each bubble enters the tube, the deep reddish-brown dioxide forms. After a few moments the color fades, owing to the fact that the dioxide reacts with the water, which at the same time rises in the tube to take the place of the gas so removed.

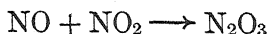
Polymeric compounds ; polymers. When the molecular weights of compounds are determined by measuring their vapor densities at temperatures not much above their boiling points, it is found that many of these vapors have molecular weights twice or more times as great as the simplest formula weight of the compound. For example, the formula of hydrogen fluoride gas is HF or H_6F_6 or an intermediate (average) value, depending upon the temperature (p. 310). Similarly, the formula of nitrogen dioxide at higher temperatures is NO_2 , and the color is reddish brown ; at lower temperatures the formula is N_2O_4 , and the color is yellow. In all such cases the simpler formula is found at the higher temperature, and at intermediate temperatures there is an equilibrium between the two forms, thus :



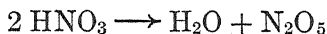
The compound of larger molecular weight is said to be a *polymeric form*, or a *polymer*, of the compound of simpler formula. Thus N_2O_4 is a polymer of NO_2 , and N_2O_4 is sometimes called *nitrogen tetroxide*, to distinguish it from the simpler form.

Nitrogen trioxide (N_2O_3). When a mixture of equal volumes of nitric oxide and nitrogen dioxide is cooled, there is obtained at first

a blue liquid, which, at a still lower temperature, freezes to a solid. The liquid, as well as the solid, is generally regarded as nitrogen trioxide:



Nitrogen pentoxide (N_2O_5). This oxide is a white crystalline unstable solid and is formed when nitric acid is treated with a strong dehydrating agent, such as phosphorus pentoxide:



The assimilation of nitrogen by plants. Our bodies must depend for life on compounds of nitrogen, but are not able to assimilate directly the free nitrogen in the atmosphere. They obtain their supply in the form of compounds of nitrogen (*proteins*) present in such foods as milk, eggs, meat, beans, and peas. Plants do somewhat better, for some of them are able, by indirect means, to utilize free nitrogen.

It has long been known that a few plants, and especially those belonging to the *legume* family, such as beans, clover, alfalfa, and peas, not only thrive in poor soil but enrich the soil in which they grow. These plants are able to do this because of the presence in the soil of certain *nitrogen-fixing* bacteria. When a legume begins to grow in a soil which contains these bacteria, the bacteria will enter the root cells and multiply with great rapidity, forming the well-known nodules on the roots of legumes (Fig. 235). These bacteria are parasitic and obtain their food from the plant, assimilating a part of it into their own tissues and oxidizing a part of it. They utilize the energy thus available in building up nitrates from the free nitrogen absorbed by the soil from the atmosphere. The nitrates are assimilated by the plant and converted to plant protein. It is

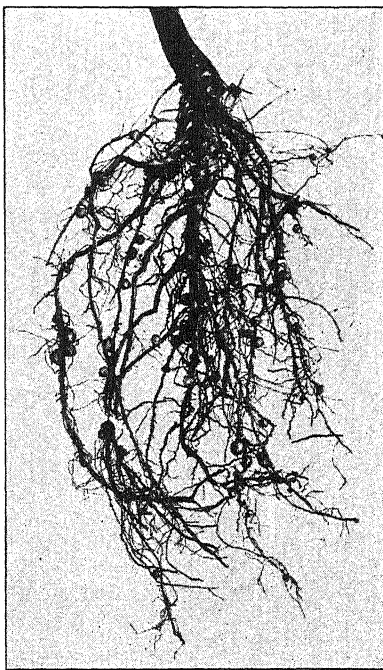


FIG. 235. Nodules on Roots of a Soybean Plant

a sort of co-operative enterprise, in which the legume furnishes the home and food for the bacteria, and the bacteria in turn furnish the plant with one of its essential foods.

The nitrogen cycle. When an animal eats plant protein this protein is changed by digestion into nitrogen compounds called *amino acids*, which are rebuilt into animal protein tissues. These in turn are eventually converted, by digestion and other processes, into such animal waste products as urea and ammonia.

In addition to the nitrogen-fixing bacteria, the soil contains other kinds of bacteria. One kind, the *nitrifying bacteria*, decompose nitrogenous organic matter (such as animal wastes, and plants which have been plowed under). The nitrogen is changed first into nitrites and then into nitrates. This organic nitrogen is transformed into a form once more usable by plants. Soils that are not well aerated may contain yet a third kind of organism known as *denitrifying bacteria*, which have an effect opposite to that of the nitrifying bacteria, reducing any nitrates present into nitrites and free nitrogen (and even ammonia). While some nitrogen is thus set free (if denitrifying bacteria are present), this is offset by the fixation of nitrogen in usable form by the nitrogen-fixing bacteria, as well as by electric discharges during thunderstorms. These various changes are represented in a general way by Fig. 236. This shows that the nitrogen taken from the soil by the plant, after undergoing many changes and serving different purposes, is finally restored to the soil from which it came.

The various changes in which the nitrogen atom participates are referred to by Mellor in the following imaginative way: "Today a nitrogen atom may be throbbing in the cells of the meadow grass; tomorrow, it may be pulsating through the tissues of a living animal. The nitrogen atom afterward may rise from decaying animal refuse, and stream to the upper regions of the atmosphere, where it may be yoked with oxygen in a flash of lightning and return as plant food to the soil in a torrent of rain; or it may be directly absorbed from the atmosphere by the soil, and there rendered available for plant food by the action of bacteria. Thus each nitrogen atom has doubtless undergone a never-ceasing cycle of changes through countless aeons of time."

Other sources for nitrogen compounds in soil. The nitrogen compounds which are present in all arable soil are derived not only (1) from the decay of organic matter and (2) from the contributions of the nitrogen-fixing bacteria, but also, as mentioned above, (3) from lightning flashes. There are about seventy-five thunder-

storms in progress at different places on the earth's surface all the time; and the oxides of nitrogen, formed in the path of the lightning

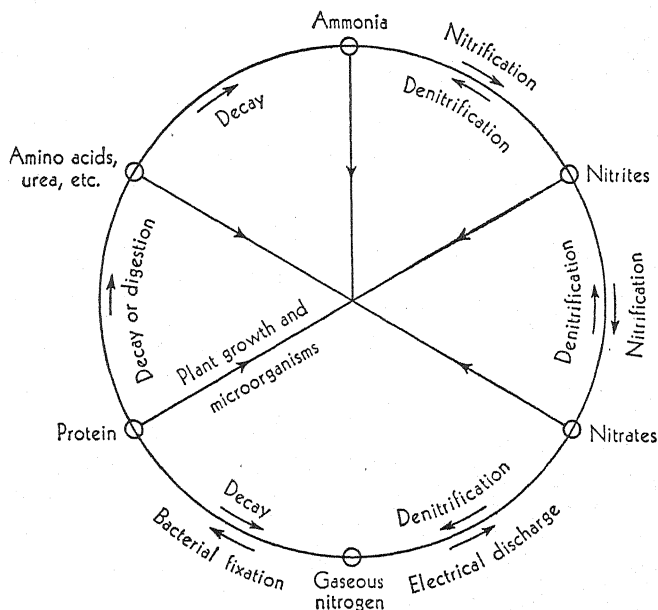


FIG. 236. *The Nitrogen Cycle*

Courtesy of the *Journal of Chemical Education*

bolts, are carried by falling raindrops into the soil. Tests conducted over a series of years in typical localities show that the fixed nitrogen added in this way amounts to about 7 lb annually per acre of ground. Finally, (4) in districts given up to agriculture large amounts of manufactured nitrogen compounds are applied to the soil as *fertilizers*, usually as sodium nitrate or ammonium sulfate or urea (made commercially from ammonia and carbon dioxide).

World production of nitrogen (in combined form). In the year 1937-1938 the world production of fixed nitrogen, either by the Haber process or some similar process, reached about 2,196,000 tons, whereas only 411,000 tons came from the destructive distillation of coal, and 224,000 tons from Chile (Fig. 237). About 87 per cent of the total went into fertilizers, and many millions of acres of otherwise worthless land were kept in productivity. Indeed, without the artificial fixation of nitrogen, which any nation can develop for itself, the present-day national policies of self-sufficiency and self-containment could hardly have been adopted with any promise of success.

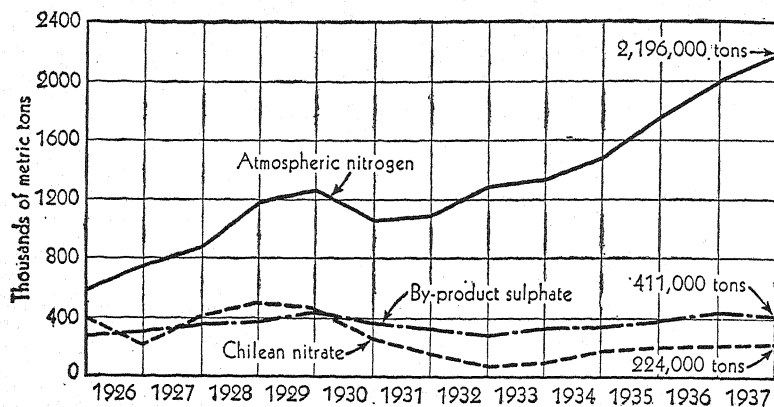


FIG. 237. World Production of Nitrogen in Combined Form.

Questions

1. If you were to open wide the valve on a container holding a large quantity of liquid ammonia at room temperature, what change in the temperature of the liquid would take place, and to what extent?
2. From the data given you about ammonia, would you infer that liquid ammonia is lighter or heavier than water?
3. Give the volume relations in each of the following reactions (use a diagram similar to Fig. 128): (a) carbon monoxide + oxygen \rightarrow carbon dioxide; (b) nitrogen + oxygen \rightarrow nitric oxide; (c) nitric oxide + oxygen \rightarrow nitrogen dioxide.
4. Why should nitric acid have been known much earlier than hydrochloric acid?
5. What is meant by the statement that nitric acid is one of the strongest of acids?
6. Hydrochloric acid was not in use before the middle of the seventeenth century. How did the alchemists make aqua regia long before that time?
7. In the preparation of nitric oxide from nitric acid and copper, would the concentration of the acid make any difference in the results?
8. Suppose a metal were found to be readily soluble in each of the following: (a) hydrochloric acid; (b) dilute sulfuric acid; (c) concentrated sulfuric acid; (d) nitric acid; (e) aqua regia; (f) water. What compound of the metal would be formed in each reaction?
9. (a) What is the difference between allotropic forms and polymeric forms? (b) Give an example of each.
10. When *concentrated* nitric acid acts on copper, the gas NO_2 is evolved. Set up oxidation-reduction equations for the reaction.

Problems

1. On the supposition that 100 per cent yields can be obtained, what volume of dry air would be required to furnish the nitrogen for the production of 100 g of nitric acid of density 1.4?
2. If you could convert all the ammonia in a liter of ammonia solution in water of density 0.88 into dry ammonia gas under standard conditions, what volume of the gas should you have?
3. What volume of dry ammonia gas, measured under standard conditions, would have to be dissolved in water to neutralize 1 l of half-normal hydrochloric acid?
4. (a) Calculate the weight of oxygen combined with 1 g of nitrogen in each of the oxides of nitrogen. (b) Show that the results conform to the law of multiple proportion.
5. One hundred grams of ammonium nitrate and of ammonium nitrite were heated in separate flasks. (a) What gas was evolved in each case? (b) Calculate the volume of each gas (under standard conditions).

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CHAPTER 22

The Nitrogen Family

	ATOMIC WEIGHT	DENSITY OF SOLID	MELTING POINT	BOILING POINT	COMPOUNDS WITH HYDROGEN AND OXYGEN
Nitrogen	14.008	1.026	- 209.9°	- 195.8°	Strong acids
Phosphorus (white)	30.98	1.82	44.1°	280°	Less strong acids
Arsenic (gray) . .	74.91	5.727	sublimes	—	Weak acids
Antimony	121.76	6.684	630.5°	1380°	Weak acids and bases
Bismuth	209.00	9.80	271°	1470°(?)	Weak bases and acids

The group. The elements of Group V have a maximum valence of 5. The type element nitrogen is followed by a family consisting of phosphorus, arsenic, antimony, and bismuth. The acid-forming qualities, which are very strong in nitrogen and phosphorus, gradually decline with increasing atomic weight, until in bismuth they have almost entirely disappeared and are replaced by the qualities of a pronounced metal. The densities and boiling points increase with the atomic numbers, but the melting points are irregular.

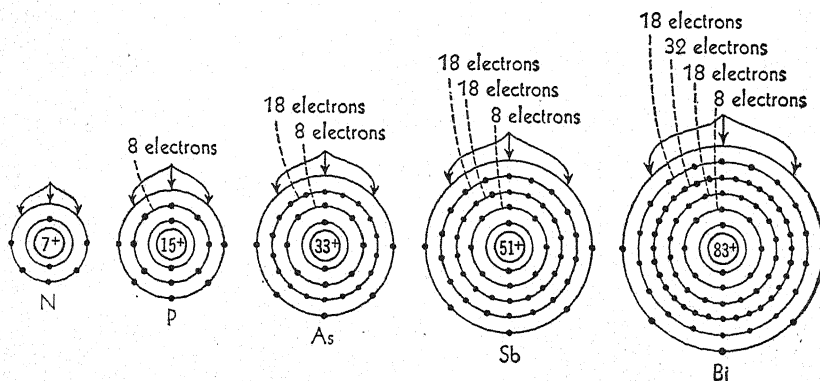


FIG. 238. *Diagrams Showing the Distribution of the Electrons in the Atoms of the Members of the Nitrogen Family. (Arrows indicate unfilled positions)*

PHOSPHORUS

History. The element phosphorus was discovered by the alchemist Brand, of Hamburg, in 1669, while he was searching for the philosophers' stone. Owing to its peculiar properties and the

secrecy which was maintained about its preparation, it remained a very rare and costly substance until the demand for it in the manufacture of matches brought about its production on a large scale. There are two fundamental allotropic forms of phosphorus, *white* (sometimes called *yellow*) *phosphorus* and *violet*, or *metallic, phosphorus*. Between these is a partially changed variety called *red phosphorus*.

White phosphorus. The usual form of phosphorus, white (or yellow) phosphorus, is really a colorless, translucent, waxy solid, which melts at 44.1° , boils at 280° , and has a density of 1.82 at ordinary temperatures. It is sold in the form of candle-like sticks, and is insoluble in water but dissolves in carbon disulfide and turpentine. It is an extremely active substance, combining directly with most of the elements, especially with oxygen. When but slightly warmed, it burns with a sputtering flame, evolving white clouds of the oxides P_4O_6 and P_4O_{10} . Because of its low kindling temperature (about 30°), it is always preserved and handled under water. It is a violent poison. Below 400° phosphorus vapor has the formula P_4 .

The slow oxidation of phosphorus. There are many peculiarities attending the slow oxidation of phosphorus. A stick lying half covered with water is slowly oxidized, and ozone is formed at the same time. Of the total oxygen used up, half goes to oxidize the phosphorus and half to combine with molecular oxygen to form ozone. The energy absorbed in the formation of the latter is furnished by the oxidation of the phosphorus. In the slow oxidation of phosphorus, light (which can be seen in a dark room) is given off, though the temperature is below the kindling temperature. This striking phenomenon suggested the name *phosphorus* ("light-bearer"); and although other materials act in a similar way, the phenomenon is called *phosphorescence*.

Red phosphorus. When white phosphorus is heated out of contact with oxygen, it is converted into a different substance, called red phosphorus. This change goes on very slowly at ordinary temperatures, is very marked at about 250° , and at 300° is quite rapid. It can be hastened by catalysts, especially by iodine or selenium. Under ordinary conditions the transition into violet phosphorus is never complete; so red phosphorus is a partially changed form and varies considerably in its properties. The pure violet form can be obtained by crystallization of phosphorus from lead.

If the red phosphorus is vaporized, it gives a vapor which is identical with that from the white form; and on condensation the latter variety is always obtained. This is in accordance with the

mersed in cold water, and hardened into sticks for the market. Low-grade phosphate rock can be used in this process.

Uses of phosphorus. The largest use of free phosphorus is in the manufacture of certain bronzes. A large percentage is also used in the preparation of certain compounds of the element. During war large amounts are used in generating smoke clouds, since phosphorus burns readily and forms a dense white smoke of oxides of phosphorus, which serves to conceal troops and ships. An important use of red phosphorus is in the *manufacture of matches*.

Matches. It has been said that the greatest discovery ever made was that of fire. Certainly one of the most useful, if not the greatest, of inventions was that of starting a fire by the use of matches. Friction matches containing phosphorus were first introduced by Walker of England about 1826. At present two general varieties are in common use, namely, the "strike-anywhere" and the safety match. In the former the materials used are (1) an oxidizing agent (potassium chlorate); (2) an oxidizable substance, such as paraffin or sulfur; (3) a binding material (glue); (4) a filling material, such as ground glass. The *tip* of the match contains, in addition to the materials mentioned above, a large percentage of phosphorus sesquisulfide (P_4S_3). By friction the phosphorus sesquisulfide ignites, and the combustion is supported by the oxidizing agent and communicated to the wood by the slowly burning paraffin. A number of other substances (starch, clay, plaster of Paris) are often used to impart desirable properties, such as resistance to moisture and regulation of speed of combustion.

In the Swedish, or safety, match, red phosphorus, an oxidizing agent, and some gritty material, such as powdered glass, are mixed with glue and placed on the side of the box. The match tip is provided with an oxidizing agent and an easily combustible substance, such as rosin and sulfur. The match cannot be ignited easily by friction except on the prepared surface of the box.

Constant working with white phosphorus frequently results in dreadful diseases of the bones of the face, while many disastrous fires are caused by accidental ignition of matches containing it. On both accounts the manufacture and use of matches containing white phosphorus is prohibited by law in all civilized countries.

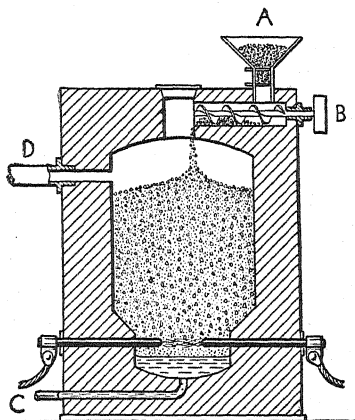
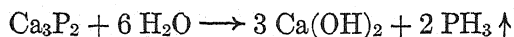


FIG. 239. Furnace for the Production of Phosphorus

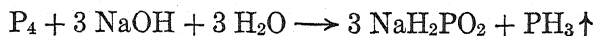
Hydrides of phosphorus — phosphine (PH_3). Phosphorus forms several compounds with hydrogen, the best known of which is *phosphine* (PH_3), the analogue of ammonia (NH_3).

Phosphine is a gas of unpleasant odor and is exceedingly poisonous. Like ammonia, it forms salts with the halogen acids. Thus, we have *phosphonium chloride* (PH_4Cl) and *phosphonium iodide* (PH_4I), analogous to ammonium chloride and ammonium iodide.

Preparation of phosphine. The simplest way of making phosphine is to treat calcium phosphide with water:



It is more conveniently made by boiling white phosphorus suspended in a concentrated solution of sodium hydroxide. The reaction is a complicated one:



Laboratory preparation. A concentrated solution of sodium hydroxide, together with several small bits of phosphorus, is placed in the flask *A*

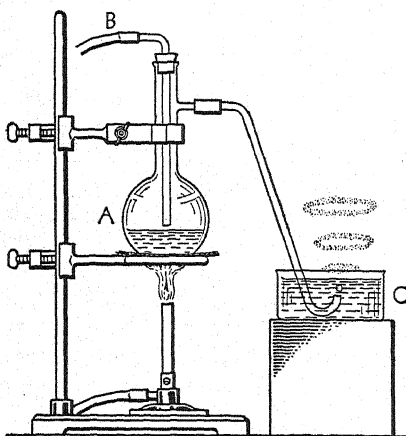
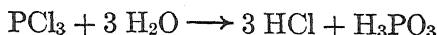


FIG. 240. *Preparation and Combustion of Phosphine*

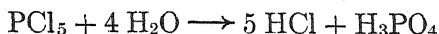
(Fig. 240), and (to remove oxygen) a current of fuel gas is passed into the flask through the tube *B* until all the air has been displaced. The gas is then turned off and the flask is heated. Phosphine is formed in small quantities, escapes through the delivery tube, and may be collected over water. If allowed to escape into the air, the exit tube should be just covered by the water in the vessel *C*. Each bubble of the gas as it escapes takes fire, and the product of the combustion (P_4O_{10}) forms beautiful rings, which float unbroken for a considerable time in quiet air. The pure phosphine does not take fire spontaneously. If prepared as above, a second hydride of phosphorus (P_2H_4) is present, which causes ignition.

Halogen compounds of phosphorus. Phosphorus forms at least two compounds with each of the halogen elements, usually of the formulas PX_3 and PX_5 . Of these, the chlorides are the most important, especially in the preparation of organic compounds. They are formed by the direct combination of phosphorus with chlorine.

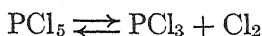
1. *Phosphorus trichloride*. This is a colorless liquid which fumes strongly in moist air, owing to the formation of *phosphorous acid*:



2. *Phosphorus pentachloride*. This is a nearly white solid, which, like the trichloride, acts on water, forming *phosphoric acid*:

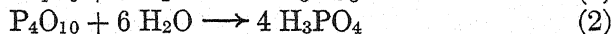
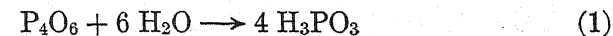


When heated, the pentachloride dissociates into the trichloride and free chlorine, which recombine on cooling:



Oxides of phosphorus. Two common oxides of phosphorus are known. (1) The formula for the molecule of *phosphorous anhydride*, or *phosphorus trioxide*, was formerly thought to be P_2O_3 but is now known to be P_4O_6 . (2) *Phosphoric anhydride*, or *phosphorus pentoxide*, is P_4O_{10} (Fig. 241). They are both white, snowlike solids. When phosphorus burns in excess oxygen or air, the pentoxide is formed; if the supply of oxygen is limited, a mixture of the two oxides results. The pentoxide is an exceedingly stable compound and has neither oxidizing nor reducing properties. It combines with water with such energy that it will thoroughly dry a moist gas passed over it. The trioxide takes up oxygen with great ease and is a strong reducing agent. Heated above 400° , it decomposes into phosphorus and phosphorus tetroxide (P_2O_4).

The acids of phosphorus. Both the trioxide and the pentoxide are typical acid anhydrides (p. 327). They combine with water directly, and the final products of the reaction are respectively *phosphorous acid* (H_3PO_3) and *phosphoric acid* (H_3PO_4):



By control of temperature and the proportion of water still other acids can be obtained from these oxides, differing from each other

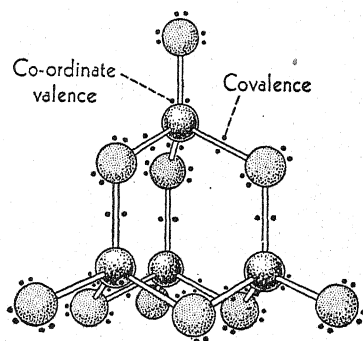


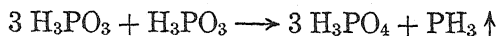
FIG. 241. Model of a Molecule of P_4O_{10}

The darker balls represent atoms of phosphorus

in the ratio between the oxide and the water. Their names, formulas, and relations are shown in the following table :

PHOSPHOROUS ACIDS		PHOSPHORIC ACIDS	
Ortho-	$\text{P}_4\text{O}_6 + 6 \text{H}_2\text{O} \longrightarrow 4 \text{H}_3\text{PO}_3$	Ortho-	$\text{P}_4\text{O}_{10} + 6 \text{H}_2\text{O} \longrightarrow 4 \text{H}_3\text{PO}_4$
Pyro-	$\text{P}_4\text{O}_6 + 4 \text{H}_2\text{O} \longrightarrow 2 \text{H}_4\text{P}_2\text{O}_5$	Pyro-	$\text{P}_4\text{O}_{10} + 4 \text{H}_2\text{O} \longrightarrow 2 \text{H}_4\text{P}_2\text{O}_7$
Meta-	$\text{P}_4\text{O}_6 + 2 \text{H}_2\text{O} \longrightarrow 4 \text{HPO}_2$	Meta-	$\text{P}_4\text{O}_{10} + 2 \text{H}_2\text{O} \longrightarrow 4 \text{HPO}_3$

The phosphorous acids. The only one of the phosphorous acids at all well known is orthophosphorous acid (H_3PO_3), commonly called simply *phosphorous acid*. It may be prepared by the action of phosphorus tribromide on water (p. 316). The pure compound forms large transparent crystals. It is generally regarded as a *dibasic* acid, although the salt Na_3PO_3 has been described. Like the trioxide from which it is derived, it is a strong reducing agent. When heated, three molecules are oxidized to phosphoric acid by the oxygen given up by a fourth molecule, thus :

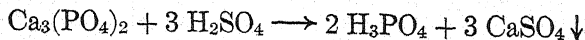


A reaction of this kind is called *autoxidation-reduction*.

Hypophosphorous acid (H_3PO_2). This acid can be prepared from the salt, NaH_2PO_2 , obtained in the preparation of phosphine (p. 404). It is a *monobasic* acid. Its salts, the *hypophosphites*, find frequent applications in medicine.

The phosphoric acids. Since all three of the phosphoric acids are derived from the stable pentoxide, it is not surprising that, like it, they should have neither oxidizing nor reducing properties.

Orthophosphoric acid (H_3PO_4). This acid is the form into which all other acids of phosphorus tend to pass when in solution, either by hydration or by oxidation. The anhydrous compound, properly called *hydrogen phosphate*, is sometimes prepared by burning white phosphorus in air and completing the oxidation with nitric acid. At present increasing amounts of the acid are prepared by burning in air the vapor of phosphorus liberated in the preparation of the element (Fig. 239) and combining the resulting oxide with water. The compound forms colorless hydrated crystals, which melt at 42.3° . For commercial purposes the acid has usually been prepared by treating calcium phosphate with concentrated sulfuric acid and filtering off the nearly insoluble calcium sulfate :

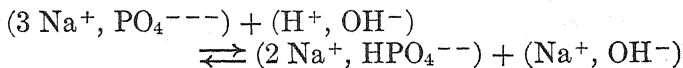


In solution, hydrogen phosphate acts as a *tribasic* acid. It is therefore capable of forming three series of salts, according as one, two, or three hydrogen atoms are replaced by metals. The formulas and the method of naming such salts are illustrated in the following table of the three sodium salts:

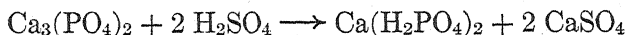
FORMULA	NAME
Na_3PO_4	Trisodium phosphate; normal, or tertiary, sodium phosphate
Na_2HPO_4	Disodium phosphate; secondary sodium phosphate
NaH_2PO_4	Monosodium phosphate; primary sodium phosphate

The heavy metals, such as silver or mercury, form only the normal, or tertiary, phosphates. Salts are also known in which there is more than one kind of cation. The most familiar ones are *micro-cosmic salt* ($\text{NaNH}_4\text{HPO}_4 \cdot 4 \text{H}_2\text{O}$) and *magnesium ammonium phosphate* (MgNH_4PO_4).

The normal salts of the alkali metals, sodium and potassium, are very strongly hydrolyzed in solution (p. 372):



Because of the alkaline character of solutions of trisodium phosphate, this salt has a wide use for cleansing purposes and for softening hard water. The normal calcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$, is only very slightly soluble. When treated with sulfuric acid it is changed into the more soluble primary salt, thus:



Advantage is taken of this reaction in the manufacture of fertilizers, so as to obtain the phosphorus in a more soluble or available form. The calcium sulfate formed seems also to add to the value of the fertilizer. Nearly one third of the total production of sulfuric acid is used for this purpose.

Pyrophosphoric acid ($\text{H}_4\text{P}_2\text{O}_7$). On heating phosphoric acid to about 225° , pyrophosphoric acid is formed in accordance with the following equation:



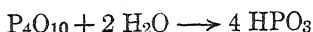
It is a white crystalline solid. Its salts can be prepared by heating a monohydrogen phosphate:



Metaphosphoric acid (glacial phosphoric acid) (HPO_3). This acid is formed when phosphoric acid is heated above 400° :



It is also formed when phosphorus pentoxide is treated with *cold* water:



Its salts are readily obtained by heating a dihydrogen phosphate:



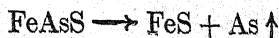
It is a white crystalline solid and is so stable toward heat that it can be fused and even volatilized without decomposition. On cooling from the fused state it forms a glassy solid, and on this account is often called *glacial* phosphoric acid. It possesses the property of dissolving small quantities of metallic oxides, with the formation of compounds which, in the case of certain metals, have characteristic colors. It is therefore used in chemical analysis for the detection of these metals.

Sulfides of phosphorus. A number of compounds consisting of phosphorus and sulfur can be obtained by heating the two elements in various proportions. The most important of these has the formula P_4S_3 , called *phosphorus sesquisulfide*. As we have seen, it is an important component in the manufacture of matches.

ARSENIC

History and occurrence. Compounds of arsenic have been known from the earliest times. The highly colored sulfides *realgar* (As_2S_2) and *orpiment* (As_2S_3) are found in nature, and have been used as pigments since the time of Aristotle. *Arsenopyrite* (FeAsS), or *mispickel*, is an abundant mineral, and the corresponding *cobaltite* (CoAsS) is not rare. The element is occasionally found in the free form, and also as the oxide As_4O_6 , called *arsenolite*. It is very widely distributed in small percentages in the sulfide ores of many metals, and these metals, as well as products prepared from the sulfur of these ores, are apt to be contaminated with arsenic. Practically all the arsenic used in the United States is obtained in the form of the trioxide As_4O_6 , as a by-product in the smelting of ores of copper and lead.

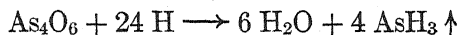
Preparation and properties. The element is prepared by subliming the natural product or by heating arsenopyrite:



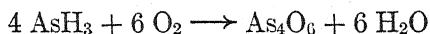
It is prepared in pure form by reducing the oxide with carbon. Like phosphorus, it occurs in several allotropic forms, the most important of which is the so-called gray, or metallic, arsenic. This is obtained as a gray crystalline mass, somewhat resembling coke in appearance, by slowly cooling the vapor of arsenic. If arsenic is heated, its vapor pressure increases rapidly and reaches 760 mm much below its melting point; consequently it sublimes without melting. All forms give the same yellowish vapor, the density of which corresponds to the molecular formula As_4 . Heated in air, arsenic forms the oxide As_4O_6 . It combines with chlorine to form the trichloride $AsCl_3$. It also combines with many of the metals, and the resulting compounds are called *arsenides*.

The element readily alloys with some of the metals, and its alloy with lead is used for making shot. The alloy is harder than pure lead, and the shot made from it is more nearly spherical. The chief use of arsenic is in the manufacture of its compounds.

Arsine (AsH_3). Whenever any compound containing arsenic is brought into the presence of nascent hydrogen, *arsine* (AsH_3) is formed, corresponding to phosphine and ammonia. The reaction when oxide of arsenic is so treated is



Arsine is a gas with a peculiar garlic-like odor and is intensely poisonous. A single bubble of the pure gas has been known to prove fatal. It is an unstable compound, decomposing into its elements when heated to a moderate temperature. It is combustible and burns with a pale, bluish-white flame to form arsenic trioxide and water when air is in excess:



When the supply of air is deficient, water and metallic arsenic are formed:



These reactions make the detection of even minute quantities of arsenic an easy problem.

Marsh's test for arsenic. Marsh's method for detecting arsenic illustrates the formation and properties of arsine. Hydrogen is generated in the flask *A* (Fig. 242) by the action of dilute sulfuric acid on zinc, is dried by being passed over calcium chloride in the tube *B*, and, after passing through the hard-glass tube *C*, is ignited at the jet *D*. If a substance containing arsenic is now introduced into the generator *A*, the arsenic is converted

into arsine by the action of nascent hydrogen and passes to the jet along with excess hydrogen. If the tube *C* is strongly heated at some point near

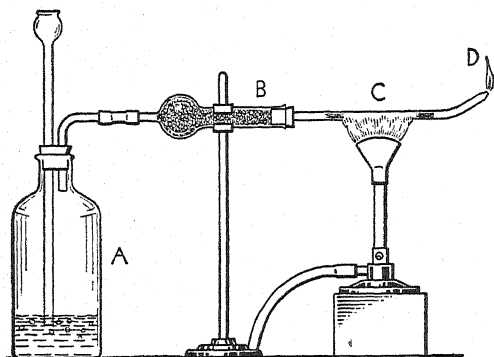


FIG. 242. Marsh's Apparatus for the Detection of Arsenic

the middle, the arsine is decomposed while passing this point, and the arsenic is deposited just beyond the heated point in the form of a shining, brownish-black mirror. A small fraction of a milligram of arsenic can be detected by this test. If the tube is not heated, the arsine burns along with the hydrogen at the jet. Under these conditions a small porcelain dish crowded down into the flame is blackened by a spot of metallic arse-

nic; for the arsine is decomposed by the heat of the flame, and the arsenic, cooled below its kindling temperature by the cold porcelain, deposits upon it as a black spot. Antimony gives a similar deposit, but it is easy to distinguish between the two.

Halogen compounds. With all four halogen elements arsenic forms low-melting, low-boiling trihalides, the best known of which is the chloride, AsCl_3 . The pentafluoride, AsF_5 , is also known. These halides are hydrolyzed by water, but not so readily as are the corresponding phosphorus compounds.

The oxides of arsenic. There are two well-known oxides of arsenic, namely, (1) *arsenious oxide* (As_2O_3), or *arsenic trioxide*, and (2) *arsenic oxide* (As_2O_5), also called *arsenic pentoxide*. Both are acid anhydrides.

1. **Arsenious oxide (arsenic trioxide).** This is the best-known compound of arsenic and is often called *white arsenic*, or simply *arsenic*. In the vapor state, as well as in the crystalline solid, its molecule has the formula As_4O_6 (Fig. 243). When metallic ores containing arsenic are smelted, the arsenic is converted into the oxide, which condenses in the flues as a fine dust from which the pure oxide may be obtained by sublimation, as it is readily volatile. The copper and lead smelters of Montana, Nevada, Utah, and Texas are the chief source of arsenic in the United States. Canada also produces much arsenious oxide from similar sources.

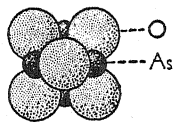


FIG. 243. The As_4O_6 Molecule

Arsenious oxide can be obtained in at least three allotropic forms. One of these is amorphous and in appearance resembles lumps of porcelain. The other two are crystalline, the more stable one being octahedral, the other rhombic. The oxide is only slightly soluble in water (the amorphous form much more so than the octahedral). It has a sweetish taste and is *extremely poisonous*, but one can accustom the system to it by gradually increased doses. In some countries the mountaineers claim that it increases their endurance in mountain-climbing, and they gradually become accustomed to daily portions much larger than a fatal dose for an ordinary person.

Arsenious oxide is the compound from which all other arsenic compounds are prepared. Its greatest use is in the preparation of insecticides and weed-killers; to some extent it is used to decolorize glass. A number of complex compounds of arsenic are used in medicine, the best known of which is *salvarsan*.

2. Arsenic pentoxide. This is a white amorphous solid whose formula is As_4O_{10} (analogous to P_4O_{10} , Fig. 241). When heated, it decomposes into the trioxide and oxygen.

Acids of arsenic. Arsenic forms two series of oxygen acids derived from the two oxides analogous to those of phosphorus. The names and formulas of these are as follows:

ARSENIOUS ACIDS	ARSENIC ACIDS
Orthoarsenious acid H_3AsO_3	Orthoarsenic acid H_3AsO_4
Pyroarsenious acid $\text{H}_4\text{As}_2\text{O}_5$	Pyroarsenic acid $\text{H}_4\text{As}_2\text{O}_7$
Metarsenious acid HAsO_2	Metarsenic acid HAsO_3

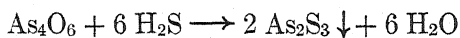
The arsenious acids. When dissolved in water, arsenic trioxide gives rise to a number of different acids, none of which has been obtained in pure condition and all of which are very weak. By suitable means the salts of these acids can be obtained; those of sodium and potassium are derived from the metarsenious acid HAsO_2 , while those of most of the other metals are derived from the ortho acid H_3AsO_3 . Thus the potassium salt is KAsO_2 , while the silver salt is Ag_3AsO_3 . Salts of the pyro acid $\text{H}_4\text{As}_2\text{O}_5$ are also known. The copper salts are of importance. *Scheele's green* (CuHAsO_3) is used as a pigment. *Paris green* is used as a poison for insects. It is generally given the formula $(\text{Cu}(\text{AsO}_2)_2)_3 \cdot \text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$, in accordance with which it must be regarded as a combination of copper metarsenite and copper acetate. Combinations of two salts are called *double salts*. Freshly precipitated ferric hydroxide adsorbs arsenic compounds and serves as an antidote for arsenic poisoning.

The arsenic acids. When arsenic trioxide is boiled with nitric acid and the solution is evaporated to a sirup, crystals of orthoarsenic acid, $2 \text{H}_3\text{AsO}_4 \cdot \text{H}_2\text{O}$, are obtained. Salts of this acid are not infrequently found in nature, and many have been prepared in the laboratory. Calcium arsenate, $\text{Ca}_3(\text{AsO}_4)_2$, and lead arsenate are widely used insecticides. The reddish-brown silver salt, Ag_3AsO_4 , and the magnesium ammonium salt, $\text{MgNH}_4\text{AsO}_4$, are of importance in analytical chemistry. All these salts are quite similar to the corresponding phosphates. Unlike phosphoric acid, arsenic acid is an oxidizing agent, as might be anticipated from the instability of its anhydride.

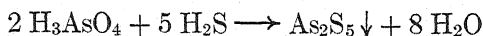
Sulfides of arsenic. There are three well-known sulfides of arsenic, namely, As_2S_2 , As_2S_3 , and As_2S_5 .

1. **Arsenic disulfide (realgar) (As_2S_2).** Realgar is a brittle red solid and can be prepared by heating arsenic and sulfur together in the proper proportions.

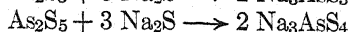
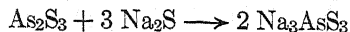
2. **Arsenic trisulfide (orpiment) (As_2S_3).** This sulfide, a yellow crystalline solid, is formed when hydrogen sulfide is passed into an acidulated solution of arsenic trioxide:



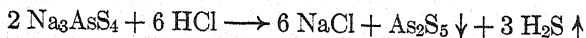
3. **Arsenic pentasulfide (As_2S_5).** This compound, along with arsenic trisulfide, forms as a yellow precipitate when hydrogen sulfide is passed into a solution of arsenic acid to which hydrochloric acid has been added:



Thio salts of arsenic. When either the trisulfide or the pentasulfide is treated with a solution of a *soluble sulfide*, such as sodium sulfide (Na_2S) or ammonium sulfide ($(\text{NH}_4)_2\text{S}$), it is dissolved; and when the solution is evaporated, well-crystallized *thio salts* are obtained:



These salts may be regarded as derived from the corresponding oxygen salts by the replacement of oxygen with sulfur. Thio salts corresponding to both the pyro and the meta acids are also known. All these salts are easier to obtain in well-crystallized form than the oxygen salts. On treatment with acids they are decomposed, with the formation of sulfides:



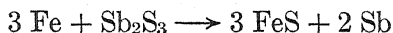
In chemical analysis these reactions make it possible to separate the sulfides of arsenic from those of other elements which are insoluble in the sulfides of sodium or ammonium.

ANTIMONY

Historical. Compounds of antimony, as well as the element itself, have been known from the earliest times. The Chaldeans appear to have made ornamental vessels of the metal. The Chinese employed preparations of antimony as drugs. The sulfide Sb_2S_3 , known as *stibnite*, was called *stibium* by Pliny; and the name *antimonium* first appears in the works of the alchemist Geber. In the fifteenth century, compounds of antimony were widely used as medicines.

Occurrence and uses. The chief ore of antimony is stibnite. This is rather widely distributed in different countries, but the supply comes principally from China, Mexico, Czechoslovakia, and Bolivia. The United States produces a small amount only.

Antimony is rarely used in the pure state, but is melted with other low-melting metals (for example, lead) to form alloys, such as type metal, Babbitt metal, and pewter. The metal may be obtained by reducing the oxide, Sb_2O_3 , with carbon or the sulfide with iron:



Properties. Like phosphorus and arsenic, antimony exists in several distinct forms, the familiar one being the ordinary gray form. The latter is a silvery, shining metal, very brittle, forming crystals which, like those of gray arsenic, belong to the hexagonal system. Its density is 6.68, its melting point 630.5° , and its boiling point 1380° . Its vapor consists of the molecules Sb_2 and Sb_4 .

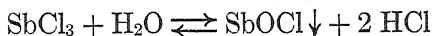
Chemical conduct. In its compounds antimony may be either quinquivalent, quadrivalent, or trivalent. In the compounds in which it is trivalent it plays the part of a metal; as a quinquivalent element it is, like arsenic, a nonmetal. *It stands midway between arsenic, which is strictly acid-forming, and bismuth, which is base-forming.* Antimony is not attacked by dilute acids (it is below hydrogen in the electromotive series). Concentrated sulfuric acid converts it into the sulfate $\text{Sb}_2(\text{SO}_4)_3$, with liberation of sulfur dioxide, and nitric acid oxidizes it to the quinquivalent condition, forming the solid H_3SbO_4 .

When heated on charcoal with a blowpipe flame, the oxide Sb_2O_3 results, and forms a characteristic bluish-white film on the charcoal. Chlorine unites with it, forming the chloride SbCl_3 .

Stibine (SbH_3). The gas *stibine* (SbH_3) is formed under conditions which are very similar to those which produce arsine, and it closely resembles the latter compound, though it is still less stable. It is very poisonous.

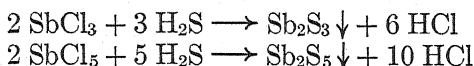
In Marsh's test for arsenic, any antimony that is present is converted into stibine and this results in a black mirror deposit, as in the case of arsenic. The deposit is more sooty in appearance than is the arsenic deposit, and it is not dissolved by a solution of sodium hypochlorite, whereas the deposited arsenic is dissolved by this reagent.

Halogen compounds of antimony. Antimony forms an almost complete double series of halogen compounds, and the pentiodide alone is unknown. They can be prepared by direct union of the elements, and in some cases by the action of the halogen acid upon antimony or its oxides. Most of these compounds are partially hydrolyzed by water, but the reaction comes to an equilibrium before it is entirely completed. With the chloride one of the products of the hydrolysis is the oxychloride SbOCl :



Oxides of antimony. Antimony forms three oxides: Sb_2O_3 , a white solid; Sb_2O_4 , a white powder; Sb_2O_5 , a yellow powder. The trioxide and pentoxide are *weak acid anhydrides and are capable of forming two series of acids corresponding in formulas to the acids of phosphorus and arsenic*. They are much weaker, however, and are of little importance.

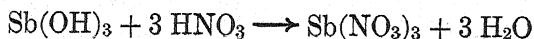
Sulfides of antimony. Antimony resembles arsenic in that hydrogen sulfide precipitates it as a sulfide when conducted into an acid solution containing an antimony compound:



The two sulfides of antimony are called the trisulfide and the pentasulfide respectively. When prepared in this way they are orange-colored substances, though the mineral stibnite is black. The sulfides of antimony are used in the manufacture of matches and of red rubber.

Thio salts of antimony. Like the sulfides of arsenic, the sulfides of antimony dissolve in solutions of soluble sulfides and form the corresponding thio salts. Of these the best known are *sodium thioantimonite* (Na_3SbS_3) and *sodium thioantimonate* (Na_3SbS_4).

Metallic properties of antimony. The fact that the sulfide of antimony is precipitated by hydrogen sulfide shows that the element can act as a metal in a chemical way. Its hydroxide, $\text{Sb}(\text{OH})_3$, dissolves in acids, forming salts, and in such reactions acts as a base:

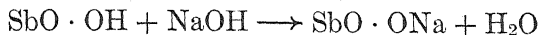


Many other reactions show that antimony has more of the chemical characteristics of a metal than of a nonmetal.

Amphoteric hydroxides. While antimony hydroxide occasionally acts as a triacid base, as represented in the last paragraph, it usually loses water and forms the monohydroxide, or oxyhydroxide, $\text{SbO} \cdot \text{OH}$:



This hydroxide differs from those we have considered in that it can act either as a weak acid or as a weak base, as indicated in the reactions

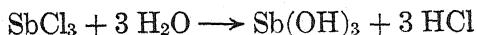


The hydroxides of a number of the metals act in this same way and are called *amphoteric hydroxides*. *Amphoteric* means "both ways," and *an amphoteric hydroxide is one that can act either as a weak acid or as a weak base*; in other words, it can yield either hydrogen ions or hydroxyl ions.

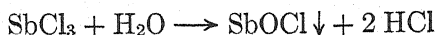
The way in which an amphoteric hydroxide will act in a given case depends on the nature of the substance with which it is reacting. In the presence of a *base* (hydroxyl ions) its hydrogen ions are used up to form water, and its ionization is displaced toward the *acid* side, so that it behaves like a *weak acid*. Similarly, in the presence of an *acid* (hydrogen ions), it acts as a *weak base*.

Oxygen acids really hydroxides. It may appear a little inconsistent to think of an acid as a *hydroxide*, but in reality nearly all oxygen acids, as well as all oxygen bases, are hydroxyl compounds. Thus, sulfuric acid is $\text{SO}_2(\text{OH})_2$ (p. 363). The real distinction between an acid and a base is not a question of the possession of hydroxyl groups, but of *the way the compound ionizes*. *If a hydroxyl compound gives hydrogen ions, it is an acid; if it gives hydroxyl ions, it is a base; if some molecules of a compound ionize one way and some the other, giving both hydrogen ions and hydroxyl ions, it is an amphoteric hydroxide*. As a rule metallic hydroxides are bases, whereas the hydroxides of nonmetals are acids.

Hydrolysis of antimony salts. Since antimony hydroxide ($\text{Sb}(\text{OH})_3$) acts as a very *weak* base, we should expect its salts to be hydrolyzed by water (p. 373). If antimony chloride were to be *completely* hydrolyzed, like phosphorus trichloride, the equation might be written as follows:



The reaction is not so complete, as only two of the three chlorine ions are replaced :



The oxychloride SbOCl , which precipitates as a white voluminous solid, may be regarded formally as arising by the loss of water from an intermediate $\text{Sb}(\text{OH})_2\text{Cl}$. The oxychloride in turn may be still further hydrolyzed by the action of a large excess of water. If we wish to prevent this hydrolysis, we must add hydrochloric acid in sufficient quantity to reverse the reaction of hydrolysis by mass action.

The antimonyl radical (SbO). The oxychloride SbOCl may be regarded as a salt of hydrochloric acid, the hydrogen atom of the acid having been replaced by the univalent *radical* SbO . This same radical is present in other salts and is termed *antimonyl*. Thus the common *tartar emetic*, used so largely in medicine, is a salt of tartaric acid ($\text{H}_2 \cdot \text{C}_4\text{H}_4\text{O}_6$) and has the formula $\text{K}(\text{SbO})\text{C}_4\text{H}_4\text{O}_6$. Its chemical name is, therefore, *potassium antimonyl tartrate*.

BISMUTH

Occurrence. Bismuth is sometimes found in the uncombined form in nature. It also occurs as oxide and sulfide and as a constituent of many rare minerals. Most of the bismuth of commerce comes from Peru and Bolivia, the production in the United States being largely restricted to the metal recovered as a by-product in refining lead. It is not an abundant element.

Preparation. Bismuth is prepared by merely heating the ore containing the native bismuth and allowing the metal to run out into suitable vessels. Other ores are converted into oxides and reduced by heating with carbon. It is difficult to prepare the metal in a high state of purity.

Properties and conduct. Bismuth is a silvery metal with a decidedly ruddy tint. It is very crystalline, brittle, and has a high luster. Its density is 9.80, its melting point is 271° , and its boiling point is about 1450° .

Bismuth dissolves in hot concentrated sulfuric and nitric acids to form bismuth salts, and it is very slowly attacked by hydrochloric acid in the presence of air. The halogen elements combine directly with it, but not with great energy.

At ordinary temperatures bismuth is not affected by air, but when heated it burns to form the yellow trioxide Bi_2O_3 , which is also

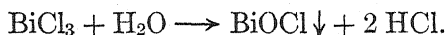
obtained by heating the hydroxide or carbonate. The chief sulfide of bismuth has the formula Bi_2S_3 . It can be prepared by direct union of the elements or by conducting hydrogen sulfide into a solution of a bismuth salt :



Prepared in this latter way it is a black amorphous precipitate.

Uses. Bismuth is used chiefly in the making of alloys and pharmaceutical preparations. The element, as well as its alloys, expands on cooling, and the alloys have low melting points. They will be referred to in connection with the metals.

Hydrolysis of bismuth salts. While the normal salts are stable in solutions containing an excess of acid, they are hydrolyzed in water or even in dilute acids. In this hydrolysis a basic salt is formed and not the hydroxide. With the chloride the reaction is expressed in the following equation :



This insoluble oxychloride may be regarded as the chloride of the base $\text{BiO} \cdot \text{OH}$, in which the group BiO plays the part of a univalent radical. This radical is called *bismuthyl*, just as the corresponding antimony radical is called *antimonyl*. There are, therefore, two series of salts: the normal salts, corresponding to the formulas BiCl_3 and $\text{Bi}(\text{NO}_3)_3$, and the bismuthyl salts (really basic salts), such as the chloride BiOCl , the nitrate BiONO_3 , and the carbonate $(\text{BiO})_2\text{CO}_3$. A number of these bismuthyl salts, particularly the nitrate and the carbonate, are used in medicine. They are usually called *bismuth subnitrate* and *bismuth subcarbonate*.

Questions

1. What explanation can you offer for the great difference between white phosphorus and violet (or red) phosphorus?
2. What economic advantages can you suggest for preparing pure (100 per cent) phosphoric acid by burning phosphorus vapor, as compared with oxidizing solid phosphorus with nitric acid?
3. What are the meanings of the prefixes *ortho-*, *meta-*, and *pyro-*, as applied to the acids of phosphorus?
4. (a) H_2S and H_2Se are decomposed by heat just as AsH_3 is. What should you expect to find if these gases were to be treated like AsH_3 in a Marsh test? (b) Would the presence of sulfides in the zinc used in the Marsh apparatus interfere with a test for arsenic?

5. What should you expect to obtain by crystallizing a mixture of trisodium phosphate and monosodium phosphate from a water solution?
6. What should you expect to get by heating arsenic pentoxide with hydrochloric acid?
7. Tabulate the interval between the melting point and the boiling point of each of the elements in this group. Can you see any periodic relations in the values you have tabulated?
8. How can you produce the following changes: (a) $P \rightarrow P_4O_{10} \rightarrow H_3PO_4 \rightarrow Na_2HPO_4 \rightarrow Na_4P_2O_7$; (b) $As \rightarrow As_2O_3 \rightarrow As_2S_3 \rightarrow Na_3AsS_3 \rightarrow As_2S_3$; (c) $Bi \rightarrow Bi_2O_3 \rightarrow BiCl_3 \rightarrow BiOCl \rightarrow Bi_2S_3$?

Problems

1. A certain phosphate rock was found to contain 80 per cent of calcium phosphate. (a) What weight of phosphorus can be prepared from 1000 kg of this rock? (b) What weight of phosphoric acid?
2. Suppose you were to prepare 100 g of metaphosphoric acid, starting with phosphorus. (a) Write equations for the reactions involved. (b) What weight of phosphorus would be required?
3. Suppose the poisonous qualities of Paris green and Scheele's green are proportional to the combined percentages of arsenic and copper in these compounds. Which one should be the more poisonous?
4. If the formula of bismuthyl carbonate is assumed to be $(BiO)_2CO_3$, what weight of bismuth will be required to make 100 g of the compound?
5. If the black mirror in the tube of a Marsh-test apparatus should be found to weigh 30 mg, what weight of "white arsenic" would be in the sample analyzed?

Reading References

- BEERY. *Stuff*. Chapter VII tells an interesting story of the safety match.
- CURTIS. "Phosphoric Acid Electrically Made at Wilson Dam," *Chemical and Metallurgical Engineering*, Vol. XLII, pp. 320-324.
- DAVIS. "Kunckel and the Early History of Phosphorus," *Journal of Chemical Education*, Vol. IV, pp. 1105-1113.
- EASTERWOOD. "Manufacture of Phosphoric Acid by the Blast Furnace Method," printed in Goldblatt's *Collateral Readings in Inorganic Chemistry*, pp. 147-157.
- FOSTER. *Romance of Chemistry*. Chapter XIV is entitled "Phosphorus and Related Elements."
- MOFFETT. "Matches," *Journal of Chemical Education*, Vol. VI, pp. 1359-1360.
- WAGGAMAN. "The Phosphate Rock Industry in the United States," *Journal of Chemical Education*, Vol. X. A series of two articles, pp. 391-395 and 476-483.
- WEEKS. *The Discovery of the Elements*. Read of the discovery of the members of the nitrogen family. (Consult the index for pages.)
- Consult the Minerals Yearbook for the production and prices of members of the nitrogen family, including phosphate rock.

CHAPTER 23

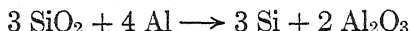
The Silicon Family; Boron

Introduction. In both families of Group IV of the periodic table the elements of smaller atomic weight are acid-forming in character, while those of greater atomic weight are metallic in their properties. At this point it is convenient to describe the acid-forming elements silicon, titanium, and zirconium (Fig. 244); carbon, as well as the more metallic elements, will be treated in later chapters. It will be appropriate to describe the trivalent element boron in connection with silicon, since it also has acid-forming properties, while the other members of Group III are metallic in character.

SILICON

Occurrence. Next to oxygen, silicon is the most abundant element. Neither the element nor its compounds are found in air, nor to any considerable extent in water, but the solid crust of the earth is estimated to contain about 27 per cent of silicon in the form of compounds. All varieties of granite, gneiss, sandstone, shale, clay, and marl contain large percentages of the element. Limestone and dolomite are the only important geological formations measurably free from it. In the realm of inorganic nature it is the central element, just as carbon is of fundamental importance in organic nature. To some extent its compounds are assimilated by certain plants and animals.

The element. In the laboratory crystallized silicon is best prepared by heating the dioxide with aluminum powder:



The silicon dissolves in the excess of melted aluminum; and when the solution has cooled and become solid, the aluminum is dissolved in hydrochloric acid, and the silicon is left in the form of shining metallic needles. The reduction of the dioxide with carbon presents the difficulty that the reduced silicon tends to combine with excess of carbon to form a carbide. This difficulty has now been overcome to a great extent, and silicon of about 98 per cent purity can be manufactured. By reducing a mixture of the oxides of silicon and

iron with carbon, an alloy of the two elements is obtained, called *ferrosilicon*. This alloy, as well as the purer silicon, has important uses in the metallurgy of iron.

Properties and conduct. The element is obtained in crystals of the isometric system, in form resembling diamond. They are very

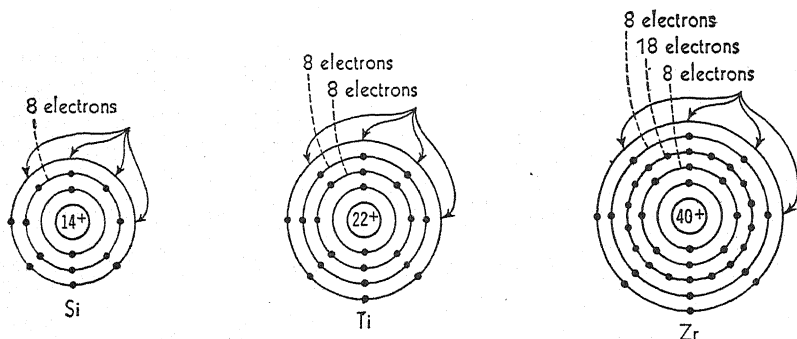
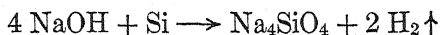


FIG. 244. *Distribution of Electrons in Atoms of the Members of the Silicon Family*

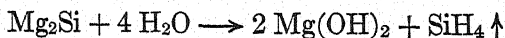
hard, easily scratching glass, and have a density of 2.4. They melt at 1420° . A lump of the element is very brittle and breaks with a crystalline fracture, which has a metallic, silvery appearance.

Silicon is readily attacked by the halogens, forming gaseous halides. The alkalis dissolve it, evolving hydrogen and forming soluble silicates — a reaction that has been used in the commercial preparation of hydrogen :

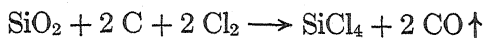


Water containing a trace of alkalis acts slowly upon it in a similar way. It is not attacked by oxygen as easily as would be expected, considering the difficulty with which its oxide is reduced. This inactivity is due to its high melting point and to the fact that a thin film of nonvolatile oxide forms upon the surface, which protects it from further action. At high temperatures it combines with the great majority of elements and forms *silicides*, such as that of magnesium (Mg_2Si).

Halogen and hydrogen compounds of silicon. A large number of compounds of silicon with hydrogen and the halogens have been prepared, and they are of interest as showing the close relationship of the element with carbon. The hydrides are formed by the action of acids or water upon a suitable silicide :



The compound SiH_4 is a colorless, combustible gas analogous to methane (CH_4). The halogen derivatives are formed by direct union of silicon with the halogens or by conducting the halogen vapor through a heated mixture of carbon and silicon oxide:



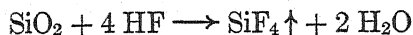
The following table shows the melting points and boiling points of a few of these silicon compounds, together with those of the corresponding carbon compounds:

Table of Some Carbon and Silicon Compounds

FORMULA	MELTING POINT	BOILING POINT	FORMULA	MELTING POINT	BOILING POINT
CH_4	- 184°	- 161.4°	SiH_4	- 185°	- 112.0°
C_2H_6	- 172°	- 89.3°	Si_2H_6	- 132.5°	- 15°
CCl_4	- 22.6°	76.8°	SiCl_4	- 70°	57.6°
C_2Cl_6	sublimes	—	Si_2Cl_6	- 1°	144°
CHCl_3	- 63.5°	61.2°	SiHCl_3	- 134°	33°
CHBr_3	7.7°	150.5°	SiHBr_3	- 60°	109°
CHI_3	119°	decomp.	SiHI_3	8°	220°

Silicon tetrachloride (SiCl_4). This is a colorless liquid which boils at 57.6° and hydrolyzes in contact with air, forming hydrochloric acid and an oxide or hydroxide of silicon. It can be made by the general method given above and also by the action of chlorine on silicon carbide (SiC). In time of war it has been used to produce smoke clouds for concealing troops and ships.

Silicon fluoride (SiF_4). Silicon fluoride is a gas at ordinary temperatures and is easily prepared by the action of hydrofluoric acid upon silicon dioxide:

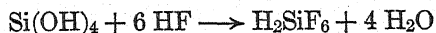


In a somewhat similar way hydrofluoric acid acts upon silicates, converting both the silicon and the metals into fluorides (p. 311).

Fluosilicic acid (H_2SiF_6). When silicon fluoride is conducted into water, it is hydrolyzed according to the following equation:



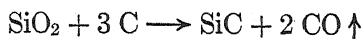
A part of the silicon hydroxide then dissolves in the hydrofluoric acid:



The soluble product H_2SiF_6 is called *fluosilicic acid*. It is a moderately

strong acid and forms soluble, well-crystallized salts with most of the metals. The potassium salt, K_2SiF_6 , is very sparingly soluble, and its formation is often employed as a test for potassium ions. Most of those elements which in the free state resemble metals, but whose chemistry is that of nonmetals, form fluo acids of the same general kind. Among these are all the elements in this group except carbon.

Silicon carbide (Carborundum) (SiC). At the temperature of the electric furnace, silicon combines with many of the metals to form binary compounds called *silicides*. It also combines with carbon to form the *carbide* SiC, best known under the trade name *Carborundum*. This carbide is made by heating sand and coke in an electric furnace — a process devised by Acheson (Fig. 245) in 1891, and extensively carried on at Niagara Falls. The reaction may be expressed in the equation



The carbide so prepared consists of beautiful black crystals, which usually have a brilliant purple iridescence. The color is due to the

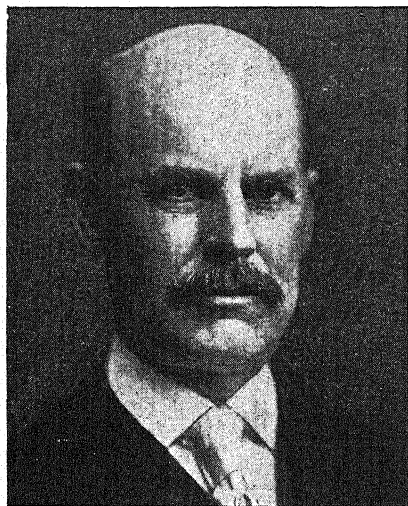


FIG. 245. *Edward Goodrich Acheson*
(1856–1931)

An American scientist who developed commercial methods for the manufacture of Carborundum, graphite, and other high-temperature products of great use in the industrial world

reflection of light from thin crystalline layers on the surface. The material is almost as hard as diamond and is much used in place of emery for grindstones and polishing powders and also in electrical resistor heaters.

Manufacture of silicon carbide.

The furnace in which silicon carbide is prepared is merely a rectangular box built of loose bricks. In the center of each end of this box is an electrode consisting of a carbon rod. The box is filled to the level of the electrodes with the charge, a layer of broken pieces of carbon is spread from one electrode to the other, and the box is then filled to the top with the charge. A cross section of a furnace so charged is represented in Fig. 246. *A* is the core of carbon, *B* the mixture of materials. These are coke, sand, a little common salt, and sawdust. The salt assists the reaction

in some way, while the sawdust chars and leaves the mass porous, thus aiding the escape of carbon monoxide gas. The broken carbon offers great resistance to the current, and the heat along the carbon core becomes intense. This causes reaction to take place from the center to some distance into the mass. The result is represented in Fig. 247. *A* is the core of carbon surrounded by a core of crystallized carbide *B*, and this in turn by a layer

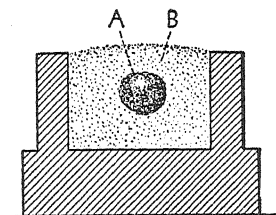


FIG. 246. Diagram Showing the Cross Section of a Charged Carborundum Furnace before Heating

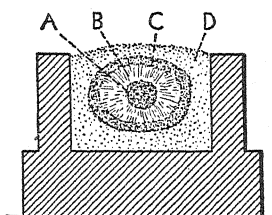


FIG. 247. Diagram Showing the Cross Section of a Charged Carborundum Furnace after Heating

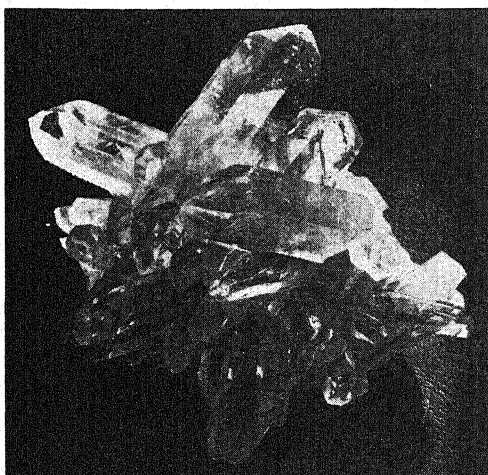
C of amorphous carbide and partially reduced products. These are known as *white stuff*, *siloxicon*, or *silundum*, according to their character. They are useful for making furnace linings and firebrick. The material *D* is unchanged.

Silicon dioxide (silica) (SiO_2). Although silicon monoxide (SiO), a solid, has been prepared in the electric furnace, the dioxide (SiO_2), called *silica*, is far better known. Practically all the silicon of nature occurs either as the dioxide itself or as its derivatives, so that it is a most important substance. The most common crystalline form is that known as *quartz* (Fig. 248). It forms beautiful colorless crystals belonging to the hexagonal system, which are sometimes of great size. A single one found in California weighed over a ton.

Quartz crystals, when pure, are colorless. Often small percentages of impurities are present which color the crystals. Some colored varieties are given special names. Thus, *amethyst* is quartz colored violet by a trace of an oxide of manganese, whereas *milky quartz* owes its characteristic appearance to the minute air bubbles present. Other varieties of silicon dioxide, some of which also contain water of hydration, are *chalcedony*, *onyx*, *jasper*, *opal*, *agate*, and *flint*. *Sand* and *sandstone* are largely silicon dioxide. It is present also in granite and gneiss.

Quartz has a density of 2.65 and is hard enough to scratch glass and most metals. It is therefore used for grinding and polishing purposes. Silica is very difficult to melt, but at the temperature of

the oxygen-hydrogen flame (above 1700°) it softens to a viscous liquid resembling melted glass. This can be drawn into threads or fashioned into laboratory utensils, such as crucibles or flasks, which have many desirable qualities. They are not attacked by most reagents, and, because of the fact that silica has a very small coefficient of expansion with temperature, they can be heated to redness and plunged into water without danger of cracking. Unfortunately quartz vessels are very expensive (Fig. 249).

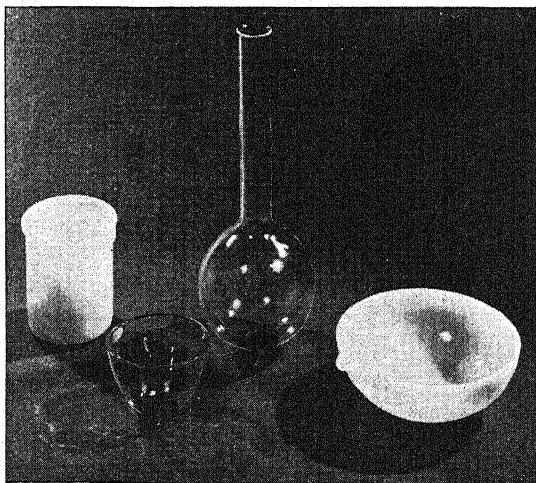


Ward's Natural Science Establishment
FIG. 248. *Quartz Crystals*

grinding stone objects, in which a dust of silica particles is formed. These particles are very sharp and insoluble. Inhaled into the throat and lungs, dust of this kind results in the serious industrial disease called silicosis.

Varieties of crystallized silica. There are three principal crystalline modifications of silica. At about 870° there is a transition point from one variety of quartz (β quartz, Fig. 250) into *tridymite*, and at about 1470° tridymite changes into *cristobalite*, which is octahedral in form. Its crystal lattice is shown in Fig. 251. The melting point of silica is therefore the melting point of cristobalite and is given as 1710° . It is very hard to determine with precision, because the melted silica is exceedingly viscous and tends to undercool into a glass.

Silicosis. There are many industrial operations, such as drilling blastholes and



The Thermal Syndicate, Ltd.
FIG. 249. *Laboratory Utensils Made of Fused Quartz*

In reality there are two forms of quartz, three of tridymite, and two of cristobalite, making seven forms in all of crystallized silica.

Chemical conduct. Silica is almost insoluble in water (except when the water is superheated) and in most acids. It is very stable,

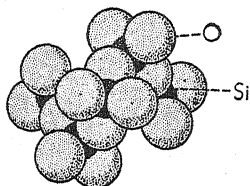


FIG. 250. Crystal Lattice of β Quartz

so that the oxygen which it contains can be removed only by the most powerful reducing agents and at very high temperatures. Hydrofluoric acid attacks it readily. Since it is the anhydride of an acid, it dissolves in fused alkalis to form *silicates*.

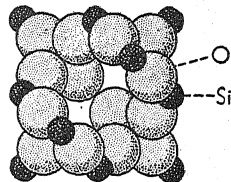
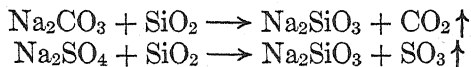
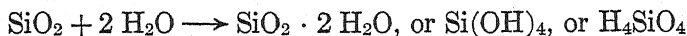


FIG. 251. Crystal Lattice of One Form of Cristobalite

Being nonvolatile, it will drive out most other anhydrides when it is heated with their salts to a high temperature, especially when the silicates so formed are fusible. The following equations illustrate this property:



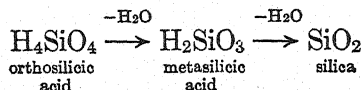
The silicic acids. 1. If finely powdered silica is heated in a bomb with water to a temperature of 400° – 500° (superheated water), it reacts with the water and goes into solution (or into what is called a *colloidal dispersion*). The product of the reaction is essentially $\text{Si}(\text{OH})_4$, called *orthosilicic acid*:



2. Orthosilicic acid may also be prepared by treating sodium silicate (Na_2SiO_3) with hydrochloric acid:



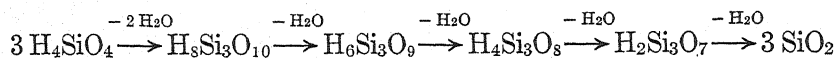
Whether the silicic acid is prepared by method 1 or method 2, if there is as much of it in the solution as 1 per cent by weight, it soon begins to "set" to a jellylike consistency. If the solution is heated so that the water will evaporate, the silicic acid is completely dehydrated, and *silica* is recovered. The equation for this dehydration reaction may be written thus:



Other supposed silicic acids and their salts. It seems possible that the dehydration may occur in much gentler stages by the splitting off of water molecules from more than one molecule of silicic acid, thus :



These hypothetical acids are called *disilicic acids*; and a series of *trisilicic acids* may also be imagined :



When two or more molecules of an acid lose water in this way, the resulting acids, such as the ones represented above, are called *condensed acids*, or *polyacids*, the ones just formulated being *condensed silicic acids*, or *polysilicic acids*. To a greater or less extent this tendency is observed with nearly all oxygen acids, and we have already had illustrations in the pyroacids of phosphorus and arsenic.

Although none of these supposed compounds of silicon has been isolated, and much less purified, they have a theoretical interest because, in a formal way, the natural mineral silicates may be thought of as being the salts of these acids. For instance, *willemite* (Zn_2SiO_4) is an orthosilicate, *wollastonite* (CaSiO_3) is a metasilicate, *leucite* (KAlSi_2O_6) is a disilicate, and *albite* ($\text{NaAlSi}_3\text{O}_8$) is a trisilicate.

But since such silicates *can actually* be formed by fusing the metallic oxides with silica in the proper proportions in dry reactions, as we have already indicated in Chapter 11, it seems somewhat more satisfactory to think of them as being *complex oxides*: *willemite* as $2 \text{ZnO} \cdot \text{SiO}_2$, *wollastonite* as $\text{CaO} \cdot \text{SiO}_2$, *leucite* as $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4 \text{SiO}_2$, and *albite* as $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6 \text{SiO}_2$.

The structure of the natural silicates. In the mineral silicates the SiO_4 ---- grouping of silicon and oxygen atoms plays a dominant role in the crystal lattice. The oxygen atoms are the largest atoms, usually much the largest atoms, present in the lattices. They pack together around the silicon atoms as SiO_4 ---- tetrahedra, and the metallic ions fit between the tetrahedra, where they can. X-ray analysis of a large number of silicates shows that there are at least five general types of piling.

1. **Separate SiO_4 ---- ions.** We should expect the SiO_4 ion to carry 4 negative charges because, if the oxygen atoms are bound to the silicon atom by covalent bonds (as we believe they are), 4 extra electrons are needed to complete the stable shells of 8 electrons around

every atom (Chap. 14). The silicon atom has 4 valence electrons, and the oxygen atom has 6. When the 4 electrons from the outside are received, the 4 pairs of shared electrons are complete (Fig. 252). These 4 electrons, of course, come from metallic atoms (or hydrogen), which, by this act, are *oxidized* to metallic ions, bearing positive charges.

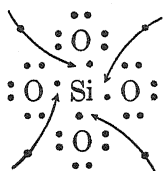
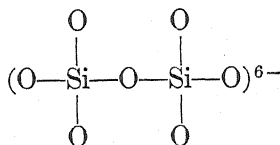


FIG. 252. Diagram Representing the Ion SiO_4^{4-}

These separate ions, SiO_4^{4-} , and the metallic ions arrange themselves in various kinds of three-dimensional checkerboard patterns of general resemblance to the $(\text{Na}^+, \text{Cl}^-)$ lattice of Fig. 99 (p. 134). *Garnet*, $\text{Ca}_3\text{Al}_2(\text{SiO}_4)_3$, or $3 \text{ CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3 \text{ SiO}_2$, crystallizes in a lattice of this type.

2. Separate, more complex silicon-oxygen ions. The ion $\text{Si}_2\text{O}_7^{6-}$ is formed when two silicon atoms share the same oxygen atom between them:



A ring-shaped ion, $(\text{Si}_6\text{O}_{18})^{12-}$, is also known (Fig. 253). Such complex negative ions as these, together with metallic ions, make up the crystal lattice. The ring ion of Fig. 253 is present in the lattice of *beryl*, $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$, or 3 Be^{++} , 2 Al^{+++} , $(\text{Si}_6\text{O}_{18})^{12-}$.

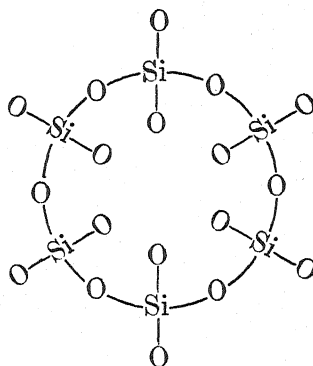
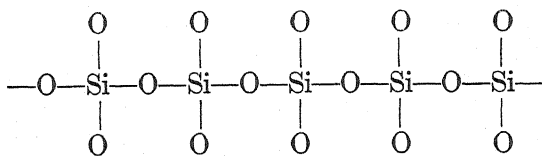


FIG. 253. Structural Formula of $(\text{Si}_6\text{O}_{18})^{12-}$

3. Silicon-oxygen strings (one-dimensional). In the picture of the lattice of β quartz (Fig. 250) zigzag silicon-oxygen chains can be noted:



Strings of this kind, or of a closely related kind, occur in all the fibrous silicates — for instance, in *tremolite*, a form of asbestos, $\text{CaMg}_3(\text{SiO}_3)_4$. These strings are extremely long and may run from

one end of the crystal fiber to the other. They are held together laterally by metallic ions (Fig. 254). The SiO_3 groups bear 2 negative

charges, $(\text{---O---Si---})^{--}$, but they do not form separate ions along the string.

4. **Silicon-oxygen sheets (two-dimensional).** The silicon and oxygen atoms also crystallize in *sheets* (Fig. 255), which are held together by positive ions located between the sheets. All the micas have this style of lattice — for example, muscovite, $\text{H}_3\text{KAl}_3(\text{SiO}_4)_3$.

5. **Silicon-oxygen nets (three-dimensional).**

Finally, the silicon and oxygen atoms often crystallize in a continuous three-dimensional network, with the metallic ions fitting into the holes. Many examples of this type are found among the feldspars — for instance, *albite*, $\text{NaAlSi}_3\text{O}_8$.

Obviously the structure of the silicates is very complicated, and we can do no more here than give an impression of the general nature of these compounds.

Silicates in solution. The ions in silicate crystals are usually bound together by very strong forces, with the result that the melting points of the silicates are nearly always quite high, and very few of the silicates are soluble in water. Among these few are sodium and potassium silicates. Sodium silicate may be prepared by fusing pure silica with sodium hydroxide or carbonate :

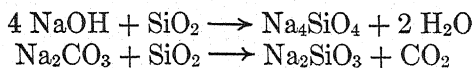
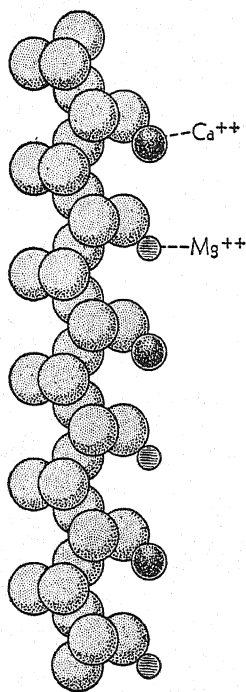
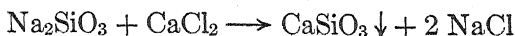


FIG. 254. *Silicon-Oxygen String in Asbestos*

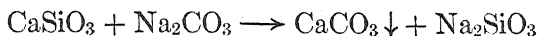
A solution of the products of such fusions in water is called *water glass*. It consists of a mixture of various silicates of sodium. When the solution is evaporated, it forms a thick liquid, which gradually hardens into a glass. It can also be brought into crystalline state. It has many uses, especially as an ingredient of soap, as a protective coating for porous surfaces (such as those of wood, plaster, or cement), and as a cement or glue, chiefly for pasteboard boxes and cartons.



When salts of the various metals are added to a solution of a sodium silicate, such as Na_2SiO_3 , insoluble silicates are precipitated:



Most natural silicates, when fused with sodium carbonate, are decomposed, and sodium silicate is formed:



The melted sodium carbonate forms a liquid in which the silicates are soluble but the carbonates are not. The insoluble carbonate is therefore precipitated. When the melt is cooled and digested with water, the sodium silicate dissolves, while the carbonate and oxides of the other metals are left undissolved. They may be filtered off and dissolved in acids. Such fusions are very frequently resorted to in chemical analysis as a means of decomposing the silicates and getting their constituents into solution, as many of them are not attacked by acids.

Fusion of the silicates. Some of the silicates have a sharp melting point and recrystallize on cooling. Many of those with a relatively low melting point resemble silica in that they fuse into a viscous liquid which, on cooling, hardens without crystallizing. If several different silicates are melted together with an excess of silica, they mix freely to a homogeneous liquid. Crystals of definite composition may separate from the melt when it is cooled, but more frequently the liquid solution simply becomes more and more viscous until it is as rigid as a true solid. Such products are called *glasses*, and they are to be regarded as very viscous solutions of one silicate in another or in silica.

The ceramic industries. A number of most important industries are based upon the silicates and the chemical transformation which they undergo. The oldest of these are the various ceramic industries, including the making of bricks, tile, terra cotta, dishes, porcelain, and glass. Cement is a more modern member of the group.

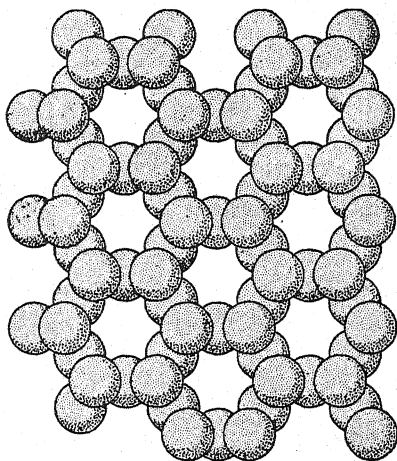


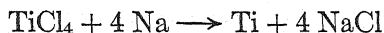
FIG. 255. *Silicon-Oxygen Sheet in Mica Showing Arrangement of the Oxygen Atoms Only*

These great industries are sometimes collectively spoken of as the *ceramic industries*. Their discussion will be delayed until a number of the compounds of the metals have been studied, especially those of sodium, calcium, and aluminum; for these elements are one or all present in all ceramic products.

TITANIUM

Occurrence. Titanium is very abundant in nature (p. 176) but is nowhere concentrated in large deposits. Its chief ores are *rutile* (TiO_2) and *ilmenite* (FeTiO_3). Our supply of these ores comes from Virginia, Arkansas, and California. In small amounts titanium is widely distributed, as is shown by the fact that out of 800 igneous rocks analyzed in the laboratory of the United States Geological Survey 748 contained titanium. It is also found as a variable constituent of certain iron ores known as *titanic iron ores*.

Preparation and properties. The element can be obtained by the reduction of the dioxide with carbon in an electric furnace. Prepared in this way, it always contains carbon and usually nitrogen and is very hard and brittle. Very pure specimens have been prepared by the action of titanium chloride on sodium in a closed steel bomb:



Its melting point (about 1800°) is above that of platinum, and its specific gravity is 4.5. It has the silvery appearance of a metal and alloys readily with many metals. An alloy known as *ferrotitanium* is made by reducing, with carbon, iron ores rich in titanium, and is used in preparing titanium steel.

The compounds. The dioxide of titanium, like that of silicon, is an acid anhydride and forms a large number of acids closely resembling the various types of silicic acids. Ilmenite (FeTiO_3) is a salt of metatitanic acid. Fluotitanic acid (H_2TiF_6) and its salts are well known.

Unlike silicon, titanium forms salts in which the element acts as a trivalent metal. The titanous salts are formed by the action of nascent hydrogen upon derivatives of the dioxide. The sulfate, $\text{Ti}_2(\text{SO}_4)_3$, and the chloride, $\text{TiCl}_3 \cdot 6 \text{H}_2\text{O}$, are examples. These salts are either green or violet in color. They are strong reducing agents.

At high temperatures titanium shows a very marked tendency to unite with nitrogen, forming the nitride, TiN . The nitride is therefore always produced in any attempt to prepare titanium in an apparatus to which

air has access, and was formerly considered to be the element itself. When iron ores containing titanium are reduced, a substance resembling crystallized copper is often found in the slag or adhering to the lining of the furnace. This also was at one time supposed to be the metal, but is really a compound containing variable amounts of titanium, carbon, and nitrogen, known as *titanium carbonitride*. It has been prepared on a large scale and used in the manufacture of *titanium tetrachloride* (TiCl_4). This chloride is a liquid boiling at 136.4° ; in contact with moist air it hydrolyzes, evolving dense clouds. The chief commercial use of titanium is the production of the white dioxide, TiO_2 . Mixed with barium sulfate, calcium sulfate, zinc oxide, or other inert white substances, it constitutes a valuable paint pigment. The chief use of rutile is as a coating on welding rods.

ZIRCONIUM

Occurrence and preparation. This is a rather rare element which occurs in nature as the oxide, ZrO_2 (*baddeleyite*), or as the well-crystallized orthosilicate, ZrSiO_4 (*zircon*). Some forms of zircon are clear white; other forms are tinted different shades of blue, yellow, or red and are used as semi-precious stones.

Australia, India, and Brazil supply nearly all the world's zircon, and little is produced in the United States. In Brazil there is a large deposit of baddeleyite, which is extensively mined. The free element can be prepared by methods similar to those used in the case of titanium. An alloy of iron and zirconium, called *ferrozirconium*, is used in the steel industry; the free element has some uses in radio tubes, in rayon spinnerets, and as a powder in flashlight mixtures.

Compounds and uses. While zirconium forms acids similar to those of silicon and titanium, particularly fluozirconic acid (H_2ZrF_6), its metallic properties are much more developed, and it forms many salts in which the element plays the part of a quadrivalent metal like tin. The hydroxide, $\text{Zr}(\text{OH})_4$, has very feeble basic properties, however, and the partial anhydride, $\text{ZrO}(\text{OH})_2$, is the base from which most of the salts are derived. Thus we have many such salts, as zirconyl chloride, ZrOCl_2 . Its most important compound is the dioxide, ZrO_2 , one of the most refractory oxides known, which fuses at about 2700° . It is used in the manufacture of crucibles which have to withstand a high temperature. It is made into bricks and sold under the name of *zircite* for use in lining furnaces. It has also been used instead of tin oxide in making enamels, glazes, and white opaque glass.

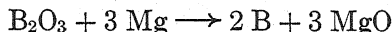
HAFNIUM

In 1923 Coster and von Hevesy discovered that zirconium is usually accompanied by a hitherto unknown element which they called *hafnium* (from an old name for Copenhagen). This element fits into the periodic table with atomic number 72 and atomic weight about 178.6, and bears a close resemblance to zirconium.

BORON

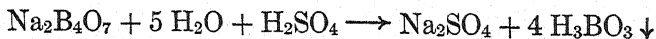
Introductory. The trivalent element boron is the first member of Group III of the periodic classification. All the other elements in this group are metals, while boron is almost wholly an acid-forming element. In its properties, as well as in those of its compounds, it strongly resembles silicon, although the formulas of the compounds of the two elements are unlike because of their difference in valence. Boron occurs in nature as *boric acid* (H_3BO_3) and in salts of various *condensed acids* (p. 426) which usually have very complicated formulas.

Preparation and properties. Boron has a great affinity for oxygen, and its oxide is difficult to reduce. It is best prepared by heating the oxide (B_2O_3) with a large *excess* of magnesium or aluminum, which metals act not only as reducing agents but as solvents for the reduced boron :



By dissolving the excess metal with acids, the crystallized boron is obtained. The crystals are usually octahedral, are exceedingly hard, and are never entirely pure. A purer specimen has been obtained by the action of hydrogen upon boron chloride at the temperature of the electric arc. Boron does not melt, but its vapor pressure (considerable at 1600°) reaches 760 mm at about 2300° . Prepared by chilling its vapor, it is an amorphous powder.

Boric acid (H_3BO_3). This compound, known also as *boracic acid*, is obtained from the waters of certain hot springs, chiefly in Italy, but, more largely, by treating a hot solution of sodium tetraborate ($\text{Na}_2\text{B}_4\text{O}_7$) with sulfuric acid. Boric acid, being but sparingly soluble in cold water, crystallizes on cooling :



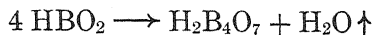
Boric acid crystallizes in pearly flakes which are slippery to the touch. It is a mild antiseptic and is sometimes used in medicine.

Its acid properties are extremely weak. When heated to fusion, it is converted into *boric oxide* (B_2O_3).

Metaboric acid and tetraboric acid. When boric acid is gently heated, it is converted into metaboric acid (HBO_2):



On heating metaboric acid to a somewhat higher temperature the condensed *tetraboric acid* ($H_2B_4O_7$) is formed:



Sodium tetraborate ($Na_2B_4O_7$). If we add sodium hydroxide to boric acid, we get a salt not of the simple acid but of the condensed tetraboric acid. This salt has the formula $Na_2B_4O_7$ and is called *sodium tetraborate*. If this salt is crystallized from hot water (above 60°), octahedral crystals of the hydrate, $Na_2B_4O_7 \cdot 5 H_2O$, are obtained. If crystallized from water at ordinary temperatures, prismatic crystals are obtained which have the formula $Na_2B_4O_7 \cdot 10 H_2O$ and are called *borax*. This is the most important compound of boron.

Borax ($Na_2B_4O_7 \cdot 10 H_2O$). Borax is found native in some arid countries, as parts of California and Tibet. It is extensively used as a constituent of glass of certain kinds, and of enamels and glazes for both metal ware and pottery. It is often used in our homes to soften hard water, as a mild alkali (like soap), and as an antiseptic.

When borax is heated, it swells up in a sort of froth, owing to the escape of steam, and this soon melts to a clear glass. The glass has the property of easily dissolving many metallic oxides, and this fact is turned to account in working with metals. When two pieces of metal are to be joined by melting them together or by the use of some kind of solder, the surfaces must be clean and free from oxide. Brass is joined by melting borax over the joint to clean the metal, and then using a low-melting brass as a solder (brazing). Metallic oxides dissolved in melted borax often color the borax glass with characteristic tints. On this account little beads of borax are used in testing for the presence of such metals.

The reason metallic oxides dissolve in borax is that borax contains an excess of acid anhydride, as can be more easily seen if its formula is written $B_2O_3 \cdot 2 NaBO_2$. The metallic oxide combines with this excess of acid anhydride, forming a mixed salt of metaboric acid.

Historical. Borax was highly valued by the alchemists and early metallurgists as a flux, a mild alkali, and for medicinal purposes. It was early obtained from alkaline salt lakes in Tibet, and later it was made from the boric acid of Italian hot springs.

It was discovered in California in 1856, but in limited quantities. Years later boron minerals were found in quantity in Death Valley (California), largely as *ulexite* ($\text{NaCaB}_5\text{O}_9 \cdot 8 \text{H}_2\text{O}$), from which borax was made, and hauled many miles to the railroad by the famous twenty-mule teams. In 1882 deposits of the crystalline rock *colemanite* ($\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5 \text{H}_2\text{O}$) were found in several places on the edges of the Mojave Desert near the railroad, and borax production in Death Valley ceased. Still later (1913) a large deposit of *kernite* ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 4 \text{H}_2\text{O}$) was discovered in the heart of the Mojave Desert and very near the railroad. This is a soluble salt, nearly pure, and needs only recrystallization for the market.

Meanwhile the search for domestic supplies of potassium compounds led to the large-scale development of the salt beds of Searles Lake (California); in the production of potassium compounds borax is obtained as a by-product. The two companies operating the kernite deposits and those of Searles Lake together produce a very large percentage of the world's boron compounds. The joint output is normally about 250,000 tons annually.

Questions

1. Write equations for the reactions that take place between water and each of the following: (a) magnesium nitride; (b) calcium phosphide; (c) magnesium silicide. (d) What term would you apply to these reactions?
2. Compare the chlorides of phosphorus, arsenic, antimony, and silicon as to (a) method of preparation; (b) reactions with water.
3. Give the formula and name of a typical member of each of the following classes of compounds: (a) monobasic acid; (b) dibasic acid; (c) tribasic acid; (d) tetrabasic acid; (e) acid salt; (f) basic salt; (g) condensed acid.
4. In what property does hydrofluoric acid differ from all other acids?
5. Some metals cannot be produced in pure form by the reduction of their oxides by carbon. Why?
6. The acids of silicon and boron are little soluble in water. On what grounds can we say that they are very weak acids?
7. Which is more abundant in the earth's crust, titanium or carbon?
8. What property of borax makes it useful (a) as a cleansing agent; (b) in brazing metals?

Problems

1. A certain mineral was found by analysis to have the following percentage composition: potassium, 14.09; aluminum, 9.69; silicon, 30.25; oxygen, 46.00. Derive a formula for the mineral.

2. What weight of Carborundum can be made from 1 ton of silicon dioxide?

3. (a) What materials are required in the preparation of silicon tetrachloride? (b) Calculate the weight of each of these required to prepare 1 kg of the chloride.

4. What volume (standard conditions) of silicon fluoride will result from the action of hydrofluoric acid on 30 g of SiO_2 ?

5. It is desired to produce a ton of ferrosilicon containing 40 per cent of silicon. (a) How much Fe_2O_3 will be required; (b) how much SiO_2 ?

6. Suppose you wished to prepare 1000 kg of borax. What weight of kernite would be required?

7. What fraction of the weight of borax is water of hydration?

Reading References

DINGLEY. "The Borax Industry in Southern California," *Journal of Chemical Education*, Vol. VIII, pp. 2113-2125. Interesting and well illustrated.

HOWARD. "Agates," *Journal of Chemical Education*, Vol. X, pp. 67-70; also an article on "Opals," Vol. XIII, pp. 553-556.

JOHNSTON. "Boron: Its Importance in Plant Growth," *Journal of Chemical Education*, Vol. V, pp. 1235-1242.

McKINNEY and MADSON. "Titanium and Its More Useful Compounds," *Journal of Chemical Education*, Vol. XIII, pp. 155-159.

TURRILL. "Studies in the Mineral and Chemical Resources of the Mojave Desert," *Journal of Chemical Education*, Vol. IX, pp. 1319-1339, 1531-1552, and 2040-2064. Three valuable articles with many illustrations.

WEEKS. *The Discovery of the Elements*. Read of the discovery of silicon and boron. (Consult the index for pages.)

The magazine *Fortune*, Vol. VI, No. 5, p. 40, tells of borax in popular style with illustrations.

The magazine *Life*, Vol. VIII, No. 14, pp. 68-69 (April 1, 1940) has an interesting article on "Silicosis."

Consult the Minerals Yearbook for the production of borates, silicates, and quartz.

The Colloidal State of Matter

The colloidal state. We all know that coarse sand shaken up with water quickly settles when we stop shaking the mixture. The finer the sand the more slowly it settles. If we powder it fine enough and then stir it into water, it will not settle at all; for the particles will be so small that they will be kept in constant motion by collision with the fast-moving molecules of the water. If we could powder the sand into individual molecules and stir them into water, we should have a true solution.

In this chapter we shall be interested in those very fine particles which are too small to settle or to be filtered from the solvent, which cannot be seen directly in even the best of microscopes, and yet which may consist of many thousands of molecules. Such particles suspended in a liquid constitute a *colloidal system*. The particles are said to be in a *colloidal state* and *dispersed* through the liquid. Moreover, we speak of the small particles as the *dispersed phase*, and the liquid as the *dispersing phase*. The term *colloidal solution* cannot fairly be used; we use the term *colloidal sol* or *colloidal dispersion* instead.

Colloids. It was formerly thought that a certain group of substances, nearly all of an amorphous character, were the only ones that could assume the colloidal state; and they were called *colloids* (Greek *kolla*, meaning "glue"). Contrasted with the colloid was the *crystalloid*, which formed a true solution and could not be obtained in the colloidal state. We now know that *any* substance can be obtained in the colloidal state in any liquid in which it is but little soluble. Some substances, however, such as starch and gelatin, have a greater tendency to assume the colloidal state than others. Although colloidal systems composed of solid particles dispersed in a liquid are the most common type, there are other types, such as liquid or solid particles dispersed in a gas and liquid particles dispersed in a liquid.

The Tyndall beam. The air in a room contains many particles of colloidal size that are too small to be seen as definite individuals even with a microscope; but if the room is dark and a beam of sunshine enters through a small hole in a curtain, these minute particles can be seen as bright, flashing points, or motes, in the sunbeam.

As a striking lecture experiment the English physicist Tyndall showed that in like manner many liquids which under ordinary circumstances appear to be perfectly clear, and even colorless, may in reality contain a great deal of finely suspended matter not removable by ordinary filtration. It is only necessary to pass a strong beam of light through the liquid, in a dark room (Fig. 256). In the absence of suspended matter the beam of light has no visible path through the liquid. In the presence of suspended matter, as in the case of the dust particles, light is reflected by these particles. All of them become visible sources of light. This bright path of light through a liquid is called the *Tyndall beam*. Although the Tyndall beam is characteristic of the colloidal state, care must be exercised in using it as a test for

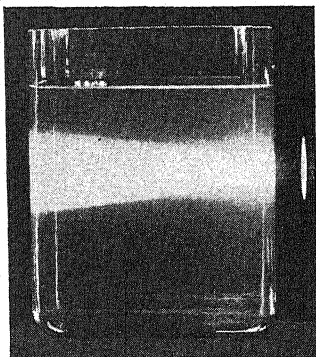


FIG. 256. Picture of a Beam of Light Shining through a Colloidal Dispersion, Showing the Tyndall Beam

the presence of colloidal matter. Dust particles in a true solution will cause it to show a Tyndall beam. Pure solvents may show a very faint Tyndall beam in the absence of colloidal matter.

Ultramicroscope. The German chemist Zsigmondy perfected an instrument, called the *ultramicroscope*, that greatly magnifies this Tyndall beam. Its essential parts are a small cell of glass or quartz to hold the colloidal dispersion, a powerful source of light to send a pencil of rays through the liquid, and a good microscope so mounted as to look upon the liquid at right angles to the beam of light and against a dark background (Fig. 24). The minute particles in the liquid are seen *not as objects* but as bright specks of light moving in zigzag paths and at greatly differing speeds (Fig. 257).

Brownian movement. As early as 1827 the English botanist Brown, while examining microscopically fine grains of pollen suspended in water, noticed that they kept up a curious zigzag motion which became known as the *Brownian movement* (p. 35 and Fig. 24); but the cause of this motion remained unexplained for eighty years. It was then shown to be a striking confirmation of our conception of the kinetic motion of the molecules of a gas or a liquid. For, if these molecules of the dispersing phase (liquid) have the high speed that we have calculated for them, their collisions with exceedingly fine particles will impart very considerable and erratic motions to those particles, even though the latter are many times as heavy as the molecules striking them.

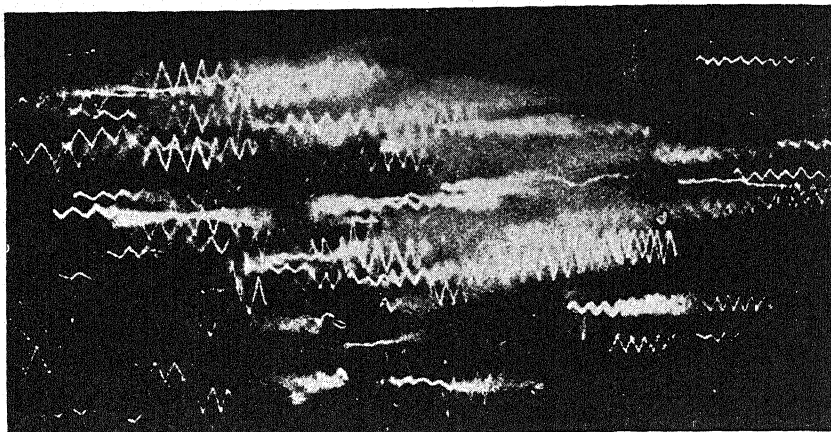


Fig. 257. Photograph Made by the Ultramicroscope, Showing Brownian Movement of Colloidal Particles Flowing Past the Field of Vision of the Ultramicroscope

Different-sized particles are indicated by the different amplitudes of vibration.
(Courtesy of Dr. P. V. Wells and Dr. Ross A. Gortner)

Size of colloidal particles. Evidently we may have in suspension particles differing widely in size. To indicate the sizes it is convenient to use a unit of length much smaller than a centimeter or a millimeter. The unit chosen is one thousandth of a millimeter and is called a *micron* (μ). Another still smaller unit, often used, is the *millimicron* ($m\mu$), which is one thousandth of a micron.

The colloidal size is somewhat arbitrarily agreed upon as lying between about $100\ m\mu$ and $1\ m\mu$. Particles smaller than $100\ m\mu$ cannot be seen in a microscope, and particles smaller than $1\ m\mu$ belong in the ordinary molecular range. Thus we may say that colloidal particles are too small to be seen microscopically, but are larger than ordinary molecules.

				Colloidal range			
1 mm	100 μ	10 μ	1 μ	100 m μ	10 m μ	1 m μ	0.1 m μ
Microscopic region				Ultramicroscopic region		Invisible	
Limit of visibility in microscope \longrightarrow						True solutions	
No perceptible Brownian movement			Particles show Brownian movement			True solutions	
Suspensions and emulsions				Colloidal sols		True solutions	

Methods of preparing colloidal dispersions. There are many ways of preparing colloidal dispersions, but all these may be classified into two groups:

1. **Dispersion methods.** We may start with an insoluble material in pieces larger than colloidal size and, by grinding or in some other way, reduce it to colloidal particles. We may then mix these particles in the desired medium. Specially designed machines, called colloid mills, are sometimes used to make colloidal dispersions in this way. Almost any sample of ocean water shows traces of gold reduced to colloidal size by the processes of nature.

In many cases we may treat finely divided solids (preferably precipitates) with some reagent that causes them to break up into a colloidal dispersion. Thus, dilute alkali causes the finer particles of clay to form a colloidal dispersion. This action is called *peptization*, and the reagent is said to *peptize* the precipitate.

2. **Condensation methods.** We may start with a substance in true solution or in the gaseous state and bring about the production of a solid or liquid in finely divided form. For example, we may add water to a solution of an oil in alcohol and throw out a cloud of colloidal oil globules; or we may pass hydrogen sulfide into a neutral solution of a salt of antimony (such as tartar emetic) and so produce colloidal antimony sulfide (Sb_2S_3); or we may add an acid to a solution of sodium thiosulfate and produce colloidal sulfur; or we may treat a very dilute solution of gold chloride with a reducing agent, such as ferrous sulfate or hydrazine chloride, and obtain colloidal gold.

It will be seen that all these processes result in gathering the atoms or molecules of an insoluble substance into clumps or droplets of colloidal size, *which then stop growing*. If growth were to continue, the clumps would become too large to be called colloidal and would form a precipitate, and the droplets would run together into large drops. Some chemists think that the formation of a colloidal dispersion is always the first step in precipitation.

Colloidal dispersion of metals. An interesting method for the preparation of a colloidal dispersion of metals was devised by the German chemist Bredig. This is really a combination of the two methods just described. Two wires of the metal, such as gold, platinum, or silver, are dipped under water, and an electric arc is struck between the ends of the wire (Fig. 258). Under these conditions some of the metal is vaporized and condensed again to particles of colloidal size. Such dispersions have intense and characteristic colors. Metals above hydrogen in the electromotive series cannot be used with water as the dispersing medium, but can be used with other liquids.

Purification of colloidal dispersions: dialysis. If we filter a colloidal dispersion through even the best of filter paper, no solid is retained on the paper; but if we use a filter made of parchment paper or animal membrane, we find that the colloidal particles are now prevented from passing through the filter. Cellophane sheets (*not* the moisture-proof variety) or cellophane sausage casings may also be used as a filter. By taking advantage of this fact we may purify a colloidal dispersion by a process called *dialysis*. The colloidal dispersion is poured into the filtering bag A, Fig. 259, and suspended from the rod B in the vessel of pure water C. Any impurities that are in true solution diffuse through the membrane, while the colloidal particles remain in the bag, and the dispersion is thus purified. Fresh water may be kept flowing continuously.

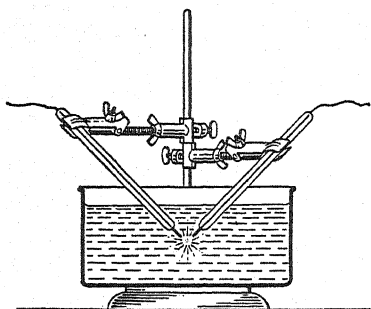


FIG. 258. Diagram Illustrating the Preparation of Colloidal Dispersions of Metals

Color of colloidal dispersions. Many colloidal systems are highly colored, but the color gives us little clue as to what is present. Minute particles of a given size absorb light waves of certain lengths and scatter others. Thus, colloidal gold may be red, blue, green, or violet, according to the size and uniformity of the particles. A little ferric chloride added to boiling water quickly hydrolyzes to a deep-red colloidal hydrated iron oxide.

It takes very little of the colloidal substance to make an intense color. A few milligrams of gold will color a liter of water. A very little of the element selenium added to glass gives it the intense red color of the automobile tail-light. Many colored glasses and glazes owe their color to colloidal material of various sorts, and many gems are colored in the same way. Periods of intensely colored sunsets follow volcanic eruptions that throw vast quantities of colloidal dust into the air.

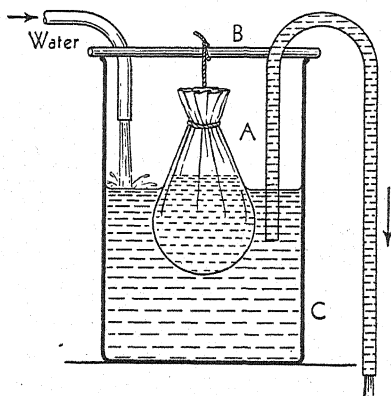


FIG. 259. Diagram Showing the Process of Dialysis

Electric charge of colloidal particles. Colloidal dispersions, even when freed of ordinary electrolytes by dialysis, are moderately good conductors and therefore contain ions. Some colloidal particles, including most of the metallic oxides, are positively charged and migrate to the cathode; others, including many metallic sulfides, gold, platinum, silver, and silicic acid, are negatively charged and migrate to the anode. It appears probable that one manner in which colloidal particles get their charges is by the adsorption of some simple ion already existing in the solution, much as a cork might "adsorb" a tack when pressed upon it. In an electric field the imprisoned ions are attracted to the electrode, dragging the whole colloidal clump along, just as the tacks would be attracted by a magnet and carry the cork along with them.

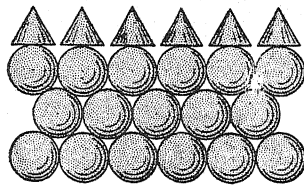


FIG. 260. *The Particles of a Solid Are Held Together by Attractive Forces Operating within the Body of the Solid*

At the surface there are free, unbalanced forces of attraction which will hold an adsorbed layer

Adsorption. By *adsorption* the chemist means the adherence of atoms, molecules, or ions of any kind to the *surface* of a solid (Fig. 260) or liquid; while by *absorption* he means the penetration of the molecules or ions into the *interior* of the solid or liquid. In the case of solids it is not easy to preserve the distinction, since so many solids are very porous.

The adsorption of an ion by a colloidal particle represents in miniature a process which goes on with masses larger than colloids and which is of importance in the arts and industries. Certain materials, such as charcoal, adsorb almost incredible quantities of gases or of liquids. Charcoal is used in gas masks to adsorb poisonous gases of certain kinds from the air. Platinum and some other metals adsorb hydrogen gas. Dried silica adsorbs water vapor and other gases. Nearly all amorphous solids adsorb most gases to some extent.

Doubtless many catalysts depend for their efficiency on their adsorbing ability, bringing the reacting substances together at high concentration within their pores, or adsorbing one component in a reversible reaction. Adsorption is sometimes *selective* in character. A given solid will adsorb some substances but not others.

Some solids suspended in solutions will adsorb dissolved materials from the liquid. The metallic oxides adsorb dyes to form *lakes* or to act as *mordants*. Fuller's earth adsorbs the coloring matter from corn (maize) oil in refining the latter for use as a salad oil.

Surface area of colloidal particles. Adsorption depends partly, at least, upon the *extent of surface* presented by the solid. Consequently the adsorptive power of any solid will depend in part upon the method of its preparation, the degree of its porosity, and the fineness of its division. It has been estimated that 1 g of high-grade adsorbing charcoal has a surface of from 100 to 1000 *square meters*.

To see how rapidly the surface area increases as a body is broken into smaller pieces, let us follow the subdivision operation shown in Fig. 261. The table lists the values of the surface area as the subdivision is continued down to colloidal size.

NUMBER OF CUBES	LENGTH OF EDGE	TOTAL SURFACE AREA
1	1 cm	6 cm ²
10 ³	1.0 mm	60 cm ²
10 ⁶	0.1 mm	600 cm ²
10 ⁹	0.01 mm	6000 cm ²
10 ¹²	1.0 μ	6 m ²
		(64.6 sq ft)
10 ¹⁵	100 mμ	60 m ²
10 ¹⁸	10 mμ	600 m ²
10 ²¹	1 mμ	6000 m ²
		(1.5 acres)

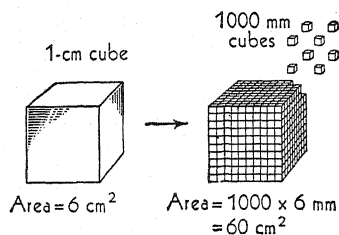


FIG. 261. A Diagram Showing Increase of Surface Area as Subdivision Increases

Coagulation of colloids. Colloidal particles of a given material carrying electric charges of the same sign tend to repel each other. This is one reason why they do not settle. This repulsion prevents the little particles from uniting to form larger ones which would ultimately produce a precipitate.

If we add an electrolyte to a colloidal dispersion, the large number of charged ions now present tends to diminish this repulsion. The charged colloidal particles attract ions of opposite sign, and the charges on the particles are thereby neutralized. Many such particles then unite to form a precipitate, and the process is called *coagulation*. The silt that deposits at the mouth of a river is due to the precipitation of the colloidal material in river water by the large concentration of salts in the water of the ocean. The amorphous precipitate so formed, made up as it is of a conglomerate of colloidal particles, has many peculiar properties and is called a *gel*.

In producing coagulation, bivalent ions are more effective than univalent ones, and trivalent ions are still more effective. This is one of the reasons why aluminum sulfate is used in the clarification of city water supplies. If we mix two colloidal systems containing

particles of opposite sign, such as colloidal iron oxide, Fe_2O_3^+ , and antimony sulfide, Sb_2S_3^- , they mutually precipitate each other in electrically equivalent quantities. Two colloidal sols (p. 436) of the same sign have no precipitating effect upon each other.

Protecting colloids. Sometimes a colloidal sol that is naturally unstable is made much more stable by the addition of some other colloidal substance of the same sign. The latter colloid, which must possess the property of being readily *peptized* (p. 439) by water, is called a *protecting colloid*. For example, the coloring matter of black ink is frequently a rather unstable colloidal sol, and gum arabic or some similar material is sometimes added as a protecting colloid to keep the coloring matter from precipitating. In making photographic plates gelatin is added to the colloidal silver salts to keep these dispersed as sols. Gelatin and gold will stick to one another. If they are dispersed in water, and if the gelatin colloidal particles are relatively small, they will coat the gold particles; but if large, they will be coated by the gold (Fig. 262).

Emulsions. If we pour together two liquids that do not dissolve in each other and shake the two violently, we get a milky-looking fluid called an *emulsion*. This consists of very minute drops of the one liquid dispersed through the other. If we let the emulsion of an oil in water stand, it will very soon separate into the original liquids from which it was made. To make an emulsion permanent we must add a third substance of a certain kind, insoluble in both the liquids. This is called the *emulsifying agent* (Fig. 263). It seems to form a little skin over the surface of the drops and prevents them from running together into big ones. Milk is an emulsion of butter fat in water, with casein as the emulsifying agent. When the milk turns sour (forming an electrolyte acid) and the casein is coagulated, the butter fat is easily collected into large lumps of butter. Most of our common disinfectants and sheep dips owe their properties to cresol emulsified in water, with a small percentage of soap as the emulsifying agent. In mayonnaise, olive oil is emulsified in water (usually with a little vinegar added) by the colloidal yolk of egg, forming a stiff, almost jellylike, product. Cod-liver-oil emulsions contain casein as the emulsifying agent. The fluids that form the

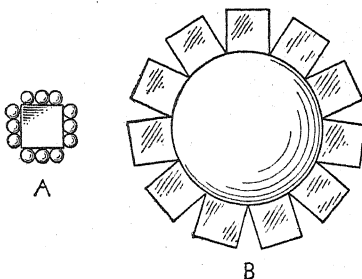
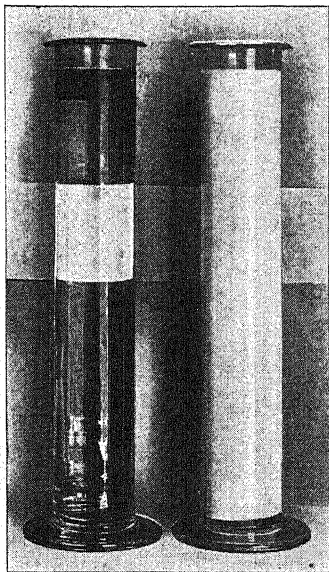


FIG. 262. (A) Gold Particles Coated with Gelatin and (B) Gelatin Particles Coated with Gold

webs of spiders and the cocoons of silkworms are secreted as emulsions that almost at once dry to form very fine filaments.



A B
FIG. 263. *Emulsions*

When oil and water are shaken together, the oil soon separates on standing (A); if a little soap is added to the oil and water, and the mixture shaken, the emulsion becomes more permanent (B)

Butter is an emulsion of water droplets in butter fat, and many lubricating greases are of this same character. The question as to which liquid forms the dispersed droplets and which is the medium for the dispersion is largely determined by the nature of the emulsifying agent employed. The agent seems to act by changing the surface tension of the two liquids to different extents, and surface tension is an important factor in emulsions. In general a water-peptizable colloid like sodium oleate will give an emulsion of oil in water, whereas an oil-peptizable colloid like calcium oleate will give an emulsion of water in oil.

Hydrophilic and hydrophobic colloids. Colloidal systems may be divided roughly into two major groups on the basis of the attraction of the colloidal particles for molecules of water, the dispersing medium. Colloidal particles for which this attraction is small, such as colloidal gold and the sulfides, are known as *hydrophobic* (water-hating) colloids. Suspensions of such colloids

do not differ greatly in viscosity from the suspending medium and are readily coagulated by electrolytes. Other colloids have a marked attraction for water and are called *hydrophilic* (water-loving) colloids. These include those substances, like gelatin and albumin, which naturally form colloidal suspensions when mixed with water. Such suspensions are generally much more viscous than pure water and are not easily coagulated by electrolytes.

Jellies. Sometimes minute colloidal particles seem to unite into threads or beads, to form a network of filamentlike structure that takes up and holds a large amount of water in much the same way that a sponge holds water. When this happens, the whole dispersion is likely to set to a more or less solid form called a *jelly*. Thus, if we

add hydrochloric acid to a solution of sodium silicate, the dilute dispersion of silicic acid sol which is first formed soon sets to a firm jelly. In fruit jellies it is a constituent of the unripe fruit, called *pectin*, that serves to form the supporting structure. In gelatin or glue the jelly may be dried out to a very compact form; but when it is dispersed in hot water and cooled, a jelly is once more obtained. When the jelly of silicic acid is dried, it forms solid, infusible lumps resembling a gum, and this cannot be dispersed by ordinary heating in water. These lumps are extremely porous, owing to the original structure of the jelly, and are very active as catalysts in many gaseous reactions. Soap is a partially dried jelly, and many minerals such as agate, flint, and opal are dry silica jellies. Photographic emulsions and many high explosives are jellies. Almost any sparingly soluble substance that does not crystallize too readily may be obtained in the form of a jelly. The so-called *solidified alcohol* consists of a porous soap and alcohol, the soap acting as a sort of sponge to hold the alcohol.

Smokes. Smoke is the dispersion of solid particles of colloidal size in a gas, particularly in air. The formation of smokes gives rise to many problems in chemical industry. When a substance such as phosphorus burns in air to form a product which is volatile at the temperature reached in combustion, but which condenses to a solid without liquefying, or when vapors are suddenly chilled below their melting points by cold air (as in distilling zinc or sulfur), the product usually forms a finely divided smoke. So, too, when dry gases combine chemically to form a solid, a smoke is usually formed; an example is the white smoke of ammonium salts that often characterizes the atmosphere of most chemical laboratories.

It is often very difficult to condense the particles of a smoke into coherent form, and this fact is of enormous industrial importance. Many precious materials literally "go up in smoke" from the stacks of smelters; much zinc is lost as a smoke of zinc oxide in brass foundries; valuable potassium compounds are lost in the smoke of cement burners; and ordinary carbon smoke causes enormous losses to individuals but corresponding profit to laundries. Sulfur trioxide (SO_3) has a powerful affinity for water, uniting with it to form sulfuric acid; yet the smoke of SO_3 , produced in the manufacture of sulfuric acid by the contact process, cannot be condensed by conducting it into pure water (save by long contact). It cost a great sum of money to learn that this smoke is rapidly absorbed only when it is conducted into concentrated sulfuric acid.

The Cottrell process. All these fine particles are electrically charged, or become so when placed in a suitable electric field. Taking advantage of this fact, Cottrell has devised a method for settling smokes that has come into wide use. The air, laden with smoke, is passed between two electrodes, one a plate and the other a series of points (Fig. 264), maintained at a high difference of electric potential. The charged particles are attracted to the plate, are discharged, and then collect into coherent dust that quickly settles. Great use is made of this process in recovering valuable materials from the stacks of smelters and from cement kilns, as well as in abating smoke nuisances (Fig. 265).

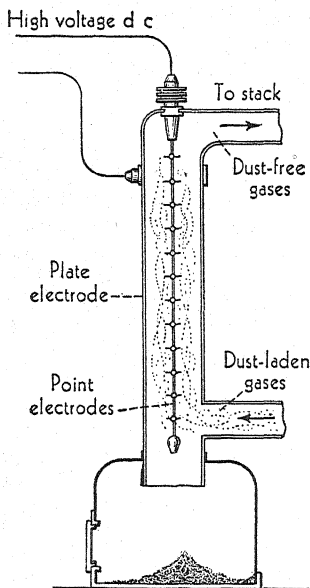


FIG. 264. Diagram of a Cottrell Precipitator

Fogs and foams. Fogs, mists, and clouds consist of very fine droplets of liquid (usually water) suspended in air, so that they correspond to *emulsions* with air as the dispersing medium. They are usually formed by contact of supersaturated vapors with dust particles; the solid particles serve as nuclei for condensation of the vapor. Foams are gas bubbles dis-

persed through a liquid — for example, whipped cream, meringue, the foam of soapy water, and the froth on beer. Sometimes these minute gas bubbles are dispersed through what we should usually consider a solid, and make it pure white. Many white flowers, like lilies, are said to owe their whiteness to dispersed gas bubbles, as does also white hair. Other examples of solids containing dispersed air bubbles are milky quartz, pumice, and lava.

The field of colloids. It will be seen that an understanding of the fundamental principles of the colloidal state is of the greatest importance. In some cases we wish to break up this condition and bring substances into true solution or to crystallization. In a very much larger number of cases the desirable properties of substances lie in the fact that they *are* colloidal, and we wish to produce or maintain this state.

Many plastic materials are in part colloidal or closely approach this condition. These include pastes, glues, gums, shellacs, varnishes, some cements, rubber, Bakelite, celluloid, clays, etc. The process of "setting" seems in many instances to involve jelly formation.

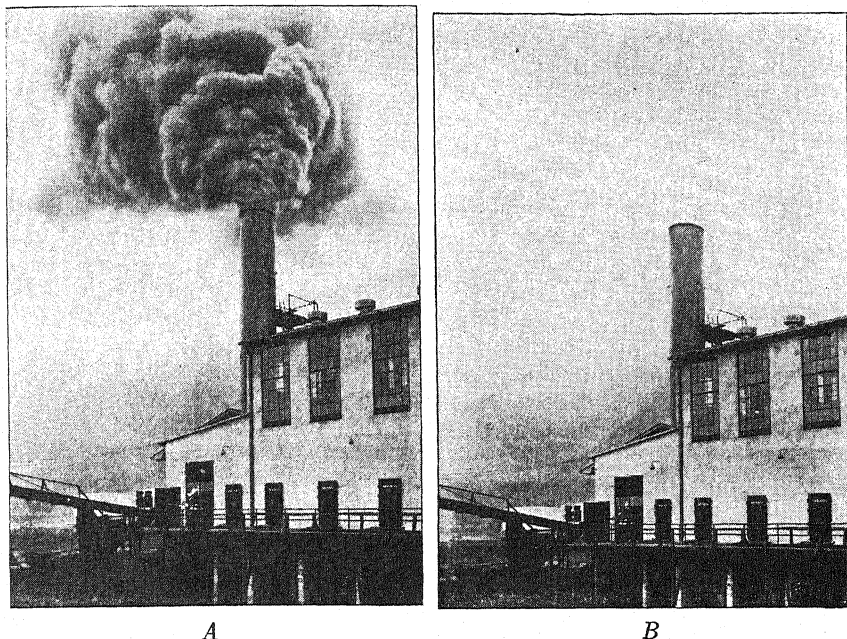


FIG. 265. *The Effect of the Cottrell Process for Abating Dust and Smoke*¹

A is a picture of a factory not equipped with any device for abating dust and smoke. *B* is a picture of the same factory after being equipped with the Cottrell precipitator

In the organic world the fundamental living cell consists of a colloidal wall enclosing a liquid dispersion very like a jelly. All organs and structures composed of cells have therefore a colloidal character. Consequently physiology and medicine deal constantly with colloidal problems, for nearly all biological processes, such as nutrition, digestion, and secretion, depend in some way upon the properties of colloids. All industries that make use of organic materials, such as the manufacture of paper, photographic plates and films, textiles, and leather, are colloidal industries.

Nearly all the food we eat, as well as the soil on which it is grown, is colloidal, so that the preparation of food of all sorts is a colloidal art. All preparation of finely divided materials, such as printer's ink and paints, involves colloidal problems. It is hard to overemphasize the importance of extending our knowledge in this field.

¹ Courtesy of the Western Precipitation Co.

Questions

1. Why does the Tyndall beam reveal the presence of particles that cannot be seen with a microscope?
2. Why should the path of a colloidal particle be a zigzag of straight lines rather than curved ones?
3. Why do the points of light in the field of an ultramicroscope move so much faster than the particles to be seen with an ordinary microscope?
4. What plan would you follow in trying to make a colloidal dispersion of zinc?
5. How does a dialyzing membrane differ from an osmotic membrane?
6. How can you prove that the particles of a colloidal dispersion are electrically charged?
7. (a) How could you prove that a hot dilute solution of ferric chloride contains colloiddally dispersed hydrated oxide of iron? (b) What reagent would you use to coagulate the dispersion?
8. The concentration of iodine ions in sea water is exceedingly small. How would you explain the fact that the ashes of some sea plants are rich in iodine (p. 317), while the ashes of others are not?
9. Many compounds used as fertilizers are very soluble in water. (a) Why are they not quickly washed out by rains? (b) What evidence have you that they wash out slowly?
10. What difference can you see between a protecting colloid and an emulsifying agent?
11. Some liquid medicinal materials, such as cod-liver oil, are often prescribed in the form of an emulsion. Can you see any advantage in this?

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Carbon and Some of Its Compounds

CARBON

Occurrence. In the free condition carbon is found in nature in several forms. Diamond is practically pure carbon, as are graphite and anthracite aside from some mineral impurities. Soft coal is a complex mixture of free carbon, together with a great variety of material derived from plant life and with mineral impurities. The natural compounds of carbon are exceedingly numerous and occur in the form of gases, liquids, and solids. Carbon dioxide (often called carbonic acid gas) is its most familiar gaseous compound. Natural gas and petroleum are composed principally of *hydrocarbons*, which are compounds of carbon and hydrogen. The carbonates, especially calcium carbonate in the form of marble and limestone, constitute great strata of rocks and are found in almost every locality. Living organisms, both plant and animal, contain a large percentage of combined carbon; and the number of its compounds which go to make up all the vast variety of animate nature is almost limitless. It is this ability of carbon to form a great variety of very complex compounds that is the chemical basis of living organisms, though compounds of other elements are also essential.

The different forms of carbon. Two forms of carbon, diamond and graphite, are highly crystalline, and are pure carbon or nearly so. The free carbon in other substances, such as coal, coke, charcoal, carbon black, and bone black, is often described as amorphous; but the free carbon in at least some of these is really microcrystalline. These various forms will be described separately.

Diamond. This form of carbon has long been known and highly prized as a gem. Diamonds are found in several localities, especially in South Africa, the East Indies, and Brazil. The crystals belong to the isometric system, and the natural crystals are always more or less imperfect. As a rule they are rough and superficially stained; to bring out the brilliancy of the gem the natural crystal is cut in such a way that the light is most effectively refracted.

Pure diamonds are perfectly transparent and generally colorless, but many are tinted a variety of colors by traces of foreign substances. Usually the colorless forms are the most highly prized, although in some

instances the color adds to the value, as in the case of the famous (blue) Hope diamond.

The weight of the diamond is expressed in carats. A carat is equal to about 0.2 g. The word *carat* is derived from a Greek word meaning "the seed, or bean, of the carob, or locust, tree." The beans were formerly used in weighing diamonds.

The largest diamond known was found in the Transvaal mines in 1905 and weighed $3025\frac{3}{4}$ carats (about 1.5 lb). This was known as the Cullinan diamond and was presented to King Edward VII by the Transvaal government. It was subsequently cut into nine large stones and a number of smaller ones. The two largest of these weigh 516.5 and $309\frac{3}{8}$ carats and are the largest cut diamonds in existence. Other famous diamonds are the Jonkers (726 carats), found in 1935 in South Africa, and the Vargas (726.6 carats), found in 1939 in Brazil. The Koh-i-noor, although weighing only $106\frac{1}{4}$ carats, is a well-known diamond because it is one of the crown jewels of England.

Composition and properties of the diamond. The density of the diamond is 3.51, and, though brittle, it is the hardest substance known. Few chemical reagents have any action upon the diamond, but when heated in pure oxygen or air it blackens and finally burns, forming carbon dioxide. Lavoisier was the first to show that carbon dioxide is formed by the combustion of the diamond in pure oxygen, thus proving that it contains carbon. Later (1814) Sir Humphry Davy showed that carbon dioxide is the sole product of the combustion, and by determining the relation between the weights of the diamond burned and the carbon dioxide produced he proved that the diamond is pure carbon.

Uses of the diamond. The great value of the diamond lies in its attractiveness as a gem. The finding of very extensive diamond fields in new localities in South Africa would have seriously threatened the commercial value of the stones had it not been that the production is a government monopoly and is strictly regulated.

The Brazilian diamonds, while well formed, are usually badly colored, sometimes almost black. The black ones are valueless as gems, but have a high value as the cutting edge of core drills and for grinding parts of machinery to a perfect fit. Diamond dust is very valuable as a polishing powder.

Artificial production of diamonds. Many attempts have been made to produce diamonds artificially. For a long time these ended in failure, for graphite, and not diamonds, was the product obtained; but in 1893 the French chemist Moissan, in his studies of high-temperature chemistry, finally succeeded in making diamonds, though they were too small to have any commercial value. He dissolved carbon in melted iron and plunged

the crucible containing the solution into water. Under these conditions the carbon crystallized in the iron in the form of diamond. The iron was then dissolved in hydrochloric acid, leaving the diamonds as an insoluble residue. By similar methods, other chemists have produced somewhat larger diamonds, but none of them is large enough to be of value as a gem.

Graphite. This form of carbon is found in nature in large quantities, especially in Ceylon and Siberia and in some localities in the United States, Mexico, and Canada. The crystals belong to the hexagonal system. Graphite is a shining black substance, very soft and greasy to the touch. Its density is about 2.25. It varies somewhat in properties, according to the locality in which it is found and the impurities present. When any form of carbon is heated in an electric furnace to a temperature of about 3500° , it rapidly vaporizes, and the vapor always condenses in the form of graphite.

Graphite is used in the manufacture of crucibles, as a lubricant, and as a protective cover for iron in the form of a paint or polish, such as stove polish. It has long been used in the manufacture of lead pencils, a fact indicated by its name, which is derived from a Greek word meaning "to write."

The commercial production of graphite. The process devised by the American chemist Acheson (Fig. 245), and carried out on a large scale at Niagara Falls, consists in heating anthracite in large electric furnaces about 40 ft in length, a longitudinal section of one of which is shown in Fig. 266. The electrodes *A, A* are made of graphite. The walls of the furnace are built of some infusible material. The furnace is nearly filled with some form of carbon, such as coarse grains of anthracite, *B*. Since coal is a poor conductor of electricity, there is placed in the center of the charge a core *C* of granulated carbon, connecting the two electrodes. The core serves to conduct the current through the charge. The charge is covered with a mixture of sand and carbon *D* (or similar materials), which serves to exclude the air. An alternating current of large amperage is supplied by the generator *G*. Under the influence of the intense heat produced by the resistance of the carbon core, the coal is changed into graphite. Prepared in this way the product is uniform in composition and free from grit, and is, as a rule, superior to the natural product.

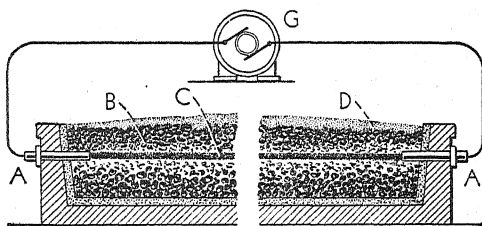


FIG. 266. *Electric Furnace for the Production of Graphite*

Crystal lattice of diamond and of graphite. Fig. 267 represents the crystal lattice of diamond, and Fig. 268 that of graphite. In order to show more clearly the relative position of the atoms in the lattice, the full volumes of the atoms have not been filled out, so that they are not shown as touching one another; the small spheres indicate merely the location of the atom centers.

In diamond (Fig. 267) it will be noted that every carbon atom is surrounded by four neighbor atoms, arranged symmetrically at the four corners of a regular tetrahedron. Every carbon atom (with a valence of four) is tied by four bonds to its four neighbors. These bonds are chemical in their nature, just like the bonds by which in its chemical compounds carbon is attached to other atoms. The great hardness of diamond argues for the strength of these bonds.

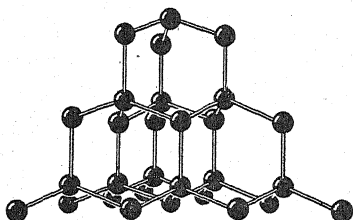


FIG. 267. *Crystal Lattice of Diamond*

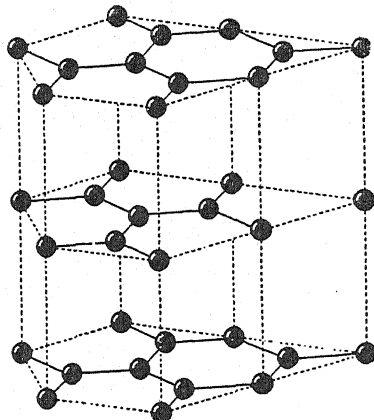


FIG. 268. *Crystal Lattice of Graphite*

It will be observed that the horizontal atom layers in the diamond lattice are not flat, but are crinkled, or puckered. In graphite, on the contrary (Fig. 268), the layers are perfectly flat, and the carbon atoms lying within these layers are tied together very rigidly by chemical bonds (valence seemingly only three) into hexagonal rings. The forces that hold one horizontal layer to the one above or below are not very strong, and consequently these layers are free to glide over one another. The "greasy," lubricating properties of graphite are due to this structure.

Coal and coke. Coals of various kinds have been formed from vast accumulations of vegetable matter, which became covered with water and earthy material and were in this way protected from oxidation. Through various geological agencies this organic matter was slowly changed into coal. In *anthracite* these changes have gone the farthest, and the carbon in this kind of coal is largely in the free condition. *Soft coals*, or *bituminous coals*, on the other hand, contain a much larger percentage of combined carbon, and *lignite* still more. When heated strongly out of contact with air, as in the

manufacture of coal gas, the carbon compounds in bituminous coal undergo complicated changes resulting in the formation of a large number of substances which are given off in the form of gases and vapors, while the mineral matter and free carbon remain behind and constitute ordinary *coke*. The process will be described more in detail in the chapter dealing with fuel gases. Both coal and coke are used not only for fuel but as reducing agents in the production of metals, especially iron and steel.

Production of coal. Coal is found and mined in nearly all industrially developed countries. The total annual production varies with the industrial prosperity of the various countries, since nearly all industries are largely dependent on coal. The chief coal-producing districts of this country include West Virginia, Pennsylvania, Illinois, Kentucky, and Ohio.

Charcoal. Charcoal is made by heating wood in the absence of air, just as coke is produced from coal under like conditions. In heating wood, just as in heating coal, many valuable volatile products are formed. In making charcoal by the older methods these products are all lost. Charcoal is now made by heating the wood in large retorts, and the volatile products are condensed and saved, as in the case of coal (Fig. 269). The mineral constituents of the wood remain in the charcoal. The relative composition of coal, coke, wood, and charcoal is represented approximately by the following analyses of typical samples:

	TOTAL CARBON	HYDRO- GEN	OXYGEN	NITRO- GEN	SULFUR	ASH	TOTAL VOLATILE MATTER
Coal (anthracite)	82.04%	2.70%	3.50%	0.77%	0.74%	10.25%	5 to 8%
Coal (semi-bituminous) . .	82.71%	4.43%	3.98%	1.33%	0.68%	6.87%	18 to 20%
Coal (bituminous)	78.03%	4.99%	6.11%	1.53%	1.05%	8.29%	30 to 35%
Wood	40.00%	7.20%	50.70%	0.80%	traces	1.30%	50 to 60%
Coke	89.00%	traces	traces	traces	0.80%	10.20%	traces
Charcoal	97.00%	traces	traces	traces	traces	3.00%	traces

Modern method for the production of charcoal. Fig. 269 shows the essential parts of a modern plant for making charcoal. The iron cars *A, A*, loaded with from one to three cords of hardwood (beech and birch), are run into the large retort *B*, and the door tightly closed. The retort is then heated slowly for about twenty-four hours by fuel burning in the fireplace *F, F*. The volatile products escape

through the pipes *C, C* and pass through the condensers *D, D*. Here are condensed those portions which are liquid at ordinary temperatures, forming a tarry liquid known as *pyroligneous acid*. This liquid, when distilled, yields *methyl alcohol* (wood alcohol), *acetic acid*,

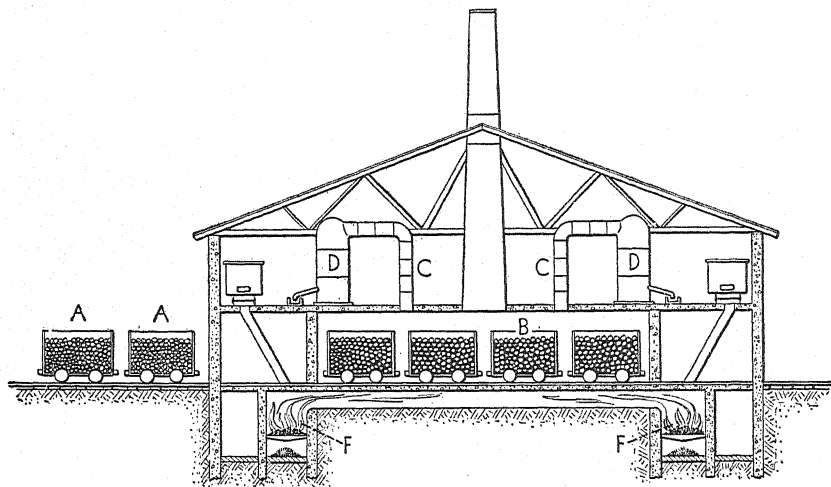


FIG. 269. Diagram of a Modern Charcoal Plant

acetone, and less important products. After the volatile matter has all been expelled from the wood, the retort is allowed to cool, and the cars containing the charcoal are run out of the retort into cooling chambers, their places in the retort being taken by other cars loaded with wood. One cord of hardwood yields about 1000 lb of charcoal.

Destructive distillation. The process of decomposing such substances as coal, wood, and bones by heating them in the absence of air is called *destructive distillation*. We say that coke, charcoal, and bone black are made by the destructive distillation of coal, wood, and bones respectively.

Bone black. This product, sometimes called *animal charcoal*, is usually classified with other forms of amorphous carbon, although it contains only about 10 per cent of carbon. It is made by the destructive distillation of bones and animal refuse. Bones are composed of about 40 per cent organic matter and 60 per cent mineral matter, chiefly calcium phosphate. After distillation the solid residue consists of finely divided carbon dispersed through the mineral matter. For some uses it is desirable that the mineral part be removed, and this is done by treatment with hydrochloric acid, which dissolves the calcium phosphate but has no action upon the

carbon. For most purposes the presence of the calcium phosphate is not objectionable and may even be of advantage.

Carbon black; lampblack. Carbon black is a black, fluffy, very finely divided powder, the particles of which are $0.025\text{--}0.05\ \mu$ in diameter. It is made by burning natural gas and directing the flame against moving metal surfaces. The unburned carbon deposits as a black soot on the metal. Its greatest use is in the manufacture of rubber goods (especially tires), to which it adds strength and resiliency. Large quantities are used in making printer's inks, paints, phonograph records, and polishes for shoes and stoves. By burning oils, coal gas, or acetylene in insufficient air a black powder (lamp-black) is obtained similar to carbon black. It has been largely replaced by carbon black.

Properties of carbon. The varieties of carbon differ in many respects, such as hardness, density, and color, owing to their crystalline condition, their fineness of division, or the presence of impurities. They are all odorless, tasteless solids insoluble in all ordinary solvents. Carbon is slightly soluble in some melted metals, and of these iron is the best solvent. Carbon cannot be melted, but at an intense heat it passes directly from a solid into a vapor.

Finely divided carbon and adsorption. Finely divided and porous carbon is remarkable for its property of adsorbing (p. 441) various gases and liquids. Charcoal from various sources and bone black are the most effective forms of carbon in this respect. The volume of the gas adsorbed depends upon the nature of the gas, on the physical state and source of the charcoal, and on the temperature and pressure during adsorption. Charcoal made from coconut shells has a very great adsorptive power for gases. Some idea of this adsorbing power may be gained from the fact that 1 volume of a certain coconut charcoal at a pressure of 760 mm adsorbs the following volumes of ammonia at the temperature indicated: 83 volumes at 70° ; 96 volumes at 50° ; 149 volumes at 20° ; and 176 volumes at 0° .

Charcoal, especially bone black, adsorbs many organic substances from their solution in water. Many dyes are adsorbed in this way, and in the manufacture of sugar the solutions are decolorized before crystallization by filtration through filters of charcoal or of bone black.

Gas masks. The use of poison gases in war has made it necessary to devise gas masks for the protection of troops. These are fitted to the face in such a way that all inhaled air has to pass through a light metal box (canister) filled with layers of various materials, the chief of which is charcoal. These materials either adsorb or combine with the poison gases, and great

efficiency is attained. Gas masks have important uses in peace times, as a defense against poisonous fumes in certain industries and in mine rescue work; and they are used by firemen in fighting fires that occasion dangerous fumes.

Activated charcoal. It has been found that the absorptive power of charcoal can be greatly increased by very carefully regulated heat treatment in the preparation of the charcoal, and then by *activating* the product by heating it in the presence of a little air or, more generally, steam. Sometimes definite catalysts are also added. Such charcoal is called *activated charcoal*.

Bancroft states that activated charcoal has been produced for use in gas masks that reduce a concentration of 7000 parts per million of chloropicrin (one of the poisons used) in a rapidly moving current of air to less than 0.5 part per million in something under 0.3 second. This high adsorptive power is due to the large surface of the charcoal. Lamb estimates that 1 cc of this charcoal has a surface of about 1000 m², or 1 cu in. a surface of 4 acres. Activated charcoal (as well as other absorbents) is used in extracting gasoline from natural gas (see *casinghead gasoline*). It is also replacing bone black in sugar-refining.

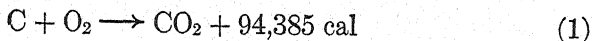
Chemical conduct. At ordinary temperatures carbon is a very inactive substance, but at higher temperatures it combines directly with most of the elements, such as oxygen, hydrogen, sulfur, silicon, chlorine, and many metals. It is a powerful reducing agent. The compounds of carbon with the metals are called *carbides*. One of the most important of these is calcium carbide (CaC₂), used in the preparation of acetylene.

CARBON MONOXIDE

NOTE. Carbon dioxide was discussed in Chapter 9 in connection with the study of the atmosphere. It would be well for the student to review this topic.

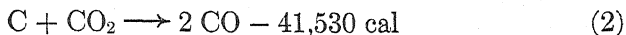
Preparation. The *extremely poisonous* compound carbon monoxide, CO, occurs in the gases issuing from volcanoes. It is formed in different metallurgical processes and especially when carbonaceous materials, such as coke, charcoal, and gasoline, are burned in a limited supply of air. The pure gas can be prepared in a number of ways, the most important of which are the following:

1. *By passing oxygen over hot carbon.* When carbon burns under ordinary conditions, the product is carbon dioxide:

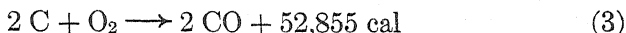


If the carbon is very hot and in great excess (in other words, if the supply of oxygen is insufficient for complete combustion), then the

carbon dioxide at first formed is reduced to carbon monoxide by the hot carbon:

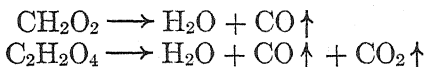


Combining equations (1) and (2), we have



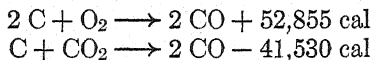
These reactions take place when hard coal burns in a stove. When the air first comes in contact with the hot coal, carbon dioxide is formed; but as this gas rises through the glowing-hot coal, it is reduced to the monoxide, which burns with a blue flame on the top of the coal, where it comes in contact with more air (Fig. 270). If the supply of air is limited, then carbon monoxide passes off as one of the products of combustion.

2. By the decomposition of formic acid or oxalic acid. In the laboratory, carbon monoxide is usually prepared either by heating formic acid (CH_2O_2) (or its sodium salt), or by heating oxalic acid ($\text{C}_2\text{H}_2\text{O}_4$):



The decomposition takes place more smoothly in the presence of sulfuric acid, which absorbs the water formed in the reaction. When oxalic acid is used, the resulting mixture of gases is passed through a solution of sodium hydroxide, which removes the carbon dioxide. The carbon monoxide is then collected over water.

Commercial manufacture of pure carbon monoxide. During 1917–1918 large quantities of pure carbon monoxide were required for the manufacture of the poison gas known as *phosgene*. Pure oxygen cannot be used to advantage in the preparation of the monoxide on a very large scale, since the heat evolved is so great as to cause serious trouble. To overcome this difficulty a mixture of oxygen and carbon dioxide was used. Both of these gases react with hot carbon to form carbon monoxide:



It will be seen from the equations above that one reaction gives out heat, while the other absorbs it. By mixing the two gases in the right proportion, therefore, the furnace in which the reactions are carried out can be kept at any desired temperature.

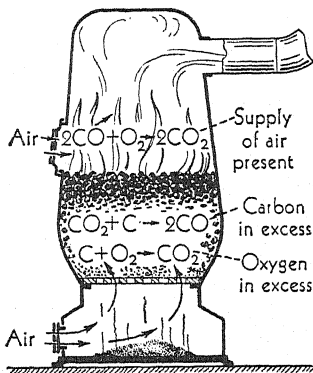
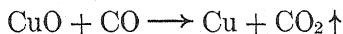


FIG. 270. The Formation of Carbon Monoxide from Hard Coal Burning in a Stove

Properties. Carbon monoxide is a colorless, practically odorless gas. It is 0.967 times as heavy as air. It can be liquefied (boiling point, -192°) and solidified (melting point, -207°). It is almost insoluble in water but is absorbed by a solution of cuprous chloride to which has been added either hydrochloric acid or ammonia. It is a fairly active compound, combining directly with a great many substances. It has a marked affinity for oxygen and burns with a blue flame:



It is therefore a strong reducing agent. For example, when it is passed over heated copper oxide, the copper is reduced to the metallic state (Fig. 271):



Carbon monoxide also combines with chlorine, sulfur, and some of the metals, such as nickel and iron.

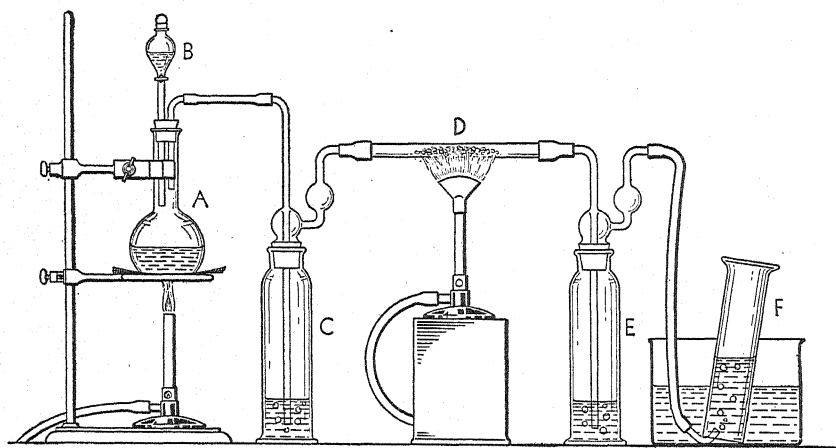


FIG. 271. Apparatus to Show the Reducing Properties of Carbon Monoxide

The reducing properties of carbon monoxide. Fig. 271 illustrates a method of showing the reducing properties of carbon monoxide. The gas is generated by gently heating some sulfuric acid in the flask *A* and then adding formic acid, a little at a time, through the funnel *B*. The bottle *C* contains water to wash the gas. *D* is a hard-glass tube containing copper oxide, which is heated by a burner. The black copper oxide is reduced to reddish metallic copper by the carbon monoxide, which is in turn changed to carbon dioxide. The

formation of the carbon dioxide is shown by the precipitate in the calcium hydroxide solution in *E*. Any unchanged carbon monoxide is collected over water in *F*.

The poisonous properties of carbon monoxide. Carbon monoxide is one of the most treacherous of poisons, since it has neither color nor odor. Its poisonous properties are explained as follows: The oxygen taken into the lungs is loosely absorbed by the red coloring matter of the blood (hemoglobin) and carried to all parts of the body to be available for oxidation. Now the affinity of this red coloring matter *for carbon monoxide is about 300 times greater than for oxygen*, and the compound formed is a stable one; consequently in an atmosphere containing even a small percentage of carbon monoxide the blood soon loses its ability to absorb oxygen, and death results. A person undergoing slight exercise in an atmosphere containing as little as 1 part of the monoxide in 500 parts of air will become unconscious in about an hour; and if such air is inhaled for three more hours, death will result.

Precautions. Since carbon monoxide is generated whenever carbon is burned in a limited supply of air, it is often formed in stoves when the air draft is shut off, especially when hard coal is used as a fuel. It is also formed when gas is burned in stoves and grates and the flame is directed against the cold metal used in the construction of the stove or the grate. *It is of the greatest importance that all stoves and grates should be provided with suitable chimney connections and that these connections should be kept in order; otherwise the carbon monoxide formed may escape into the air of the room and become a serious menace to anyone inhaling it. Many lives are lost each year because of negligence in these precautions.*

Carbon monoxide is formed in the explosion of gasoline in engine cylinders, and the exhaust gases contain from 3 to 12 per cent of the oxide. The air in a closed garage becomes dangerous when an automobile engine is allowed to run for even a few minutes, and every year *many persons lose their lives by working in a closed garage in which an engine is running.*

It is interesting that birds are very sensitive to this gas. In mine explosions carbon monoxide is always formed, and rescuers often carry canaries with them, the death of the birds warning the rescuers of their own peril (Fig. 272).

A number of tunnels have been constructed in congested districts to accommodate the automobile traffic. An effective system of ventilation is required in these tunnels to prevent the air from becoming poisoned with the carbon monoxide of automobile-exhaust gases. Extensive experiments



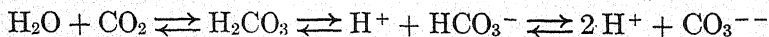
United States Bureau of Mines

FIG. 272. *Mine Rescuers Provided with Oxygen Masks, Testing for the Presence of Carbon Monoxide with Canaries*

have been carried on by the United States Bureau of Mines to determine the amount of carbon monoxide that may be present in the air of such vehicular tunnels without endangering the health of those breathing this air. These experiments showed the maximum amounts allowable to be 1 part of the monoxide in 2500 parts of air, and this only for persons breathing the air for a period not longer than one hour.

CARBONIC ACID AND SOME OF ITS SIMPLE DERIVATIVES

Carbonic acid (H_2CO_3). We have had occasion to mention carbonic acid in a number of instances and have called attention to the fact that it is a weak acid and is known only in the form of a very dilute solution. This solution is most readily prepared by passing carbon dioxide into water:



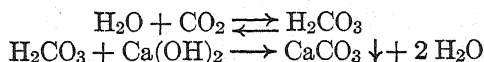
The volume of carbon dioxide absorbed in pure water is relatively small (1 volume of water at 15° and 760 mm pressure dissolves 1 volume of the gas). If, however, the water contains a base in solution, such as sodium hydroxide, the carbonic acid formed according to the equation given above reacts with the base to form the corresponding carbonate. The removal of the carbonic acid results in the union of more carbon dioxide and water, so that the absorption of carbon dioxide will continue until practically all the base has been changed into the corresponding carbonate.

Salts of carbonic acid; the carbonates. Since carbonic acid is a dibasic acid, it forms both normal and acid salts.

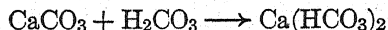
1. **Normal carbonates.** The normal carbonates are found in large quantities in nature and are often used in chemical processes. Some of these are well-known compounds. Ordinary *limestone* is a more or less impure form of calcium carbonate (CaCO_3); *marble* is nearly pure calcium carbonate in crystalline condition; normal sodium carbonate (Na_2CO_3) is the well-known *soda ash*, largely used in the manufacture of soap and glass. Among the normal carbonates only those of sodium, potassium, and ammonium are soluble in water, and these can be prepared by passing carbon dioxide into solutions of the base. The insoluble carbonates can be prepared by the general method for preparing insoluble compounds. *Since carbonic acid is such a weak acid and so readily decomposed, almost any acid will act upon a carbonate with corresponding evolution of carbon dioxide.* This reaction is used as a test for carbonates, since the carbon dioxide evolved can readily be detected.

2. **Acid carbonates.** The acid carbonates are made by treating a normal carbonate with an excess of carbonic acid. The most familiar of these is sodium hydrogen carbonate (NaHCO_3), or ordinary *baking soda*. With few exceptions they are unstable and, when heated, readily decompose even in solution. The preparation and properties of the acid carbonates may be illustrated by the following example.

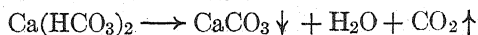
If carbon dioxide is passed into a solution of calcium hydroxide (*lime-water*), calcium carbonate at first precipitates:



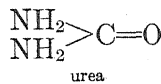
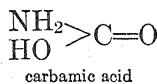
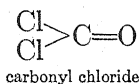
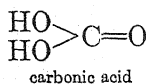
If the current of carbon dioxide is continued, however, *the precipitated calcium carbonate soon dissolves*. This is due to the formation of calcium hydrogen carbonate, which, being soluble, dissolves in the water present:



If now the solution is heated, the acid carbonate decomposes, and calcium carbonate once more precipitates :



Some simple derivatives of carbonic acid. The structural relation of carbonic acid to three of its derivatives can be seen by comparing their structural formulas :



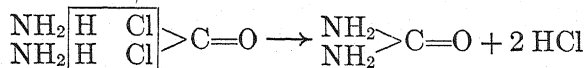
In carbonyl chloride each of the hydroxyl groups of carbonic acid has been replaced by chlorine, while in carbamic acid one hydroxyl group, and in urea both hydroxyl groups, have been replaced by the amino group NH_2 .

Carbonyl chloride (phosgene) (COCl_2). When a mixture of carbon monoxide and chlorine is exposed to the sunlight, the two gases combine, forming *carbonyl chloride*. This compound is commonly called *phosgene*, a word which means "generated by light," referring to the method of preparation. A more convenient as well as more efficient method of preparation consists in passing a mixture of carbon monoxide and chlorine over activated charcoal which acts as a catalyst. Under these conditions the two gases combine with evolution of considerable heat :

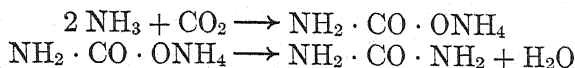


Phosgene is a colorless gas, easily condensed to a liquid boiling at 8.3° . It is used largely in the manufacture of dyes. It is very poisonous and has been used in war as a poison gas.

Urea ($\text{CO}(\text{NH}_2)_2$). In the laboratory urea can be formed by the action of carbonyl chloride upon ammonia :



Industrially, it is produced as a fertilizer by heating ammonia and carbon dioxide under pressure and at a moderately high temperature. Ammonium carbamate is an intermediate product :

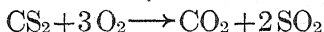


Urea is a white crystalline solid, very soluble in water. Most of the waste nitrogenous matter in the human body is eliminated in the liquid excretions as urea. An adult excretes about 30 g daily.

Carbon disulfide (CS_2). When sulfur vapor is passed over highly heated carbon, the two elements combine, forming carbon disulfide, just as carbon and oxygen unite to form carbon dioxide (Fig. 273). The reaction is endothermic, as expressed by the following equation :



Carbon disulfide is a heavy, colorless, highly refractive liquid which boils at 46.3° . When pure it has a pleasant odor, but it soon undergoes slight decomposition and acquires a most disagreeable odor. When passed through a hot tube it decomposes into its constituent elements. Its vapor is very inflammable and burns to form carbon dioxide and sulfur dioxide :



Carbon disulfide is a good solvent for many substances, such as sulfur, rubber, gums, resins, and waxes, which are not soluble in most liquids. It is also used as an insecticide and in the manufacture of carbon tetrachloride, which is so widely used as a fire-extinguisher. The vapor of the disulfide is poisonous as well as highly inflammable, so that one must exercise great care in working with it.

Cyanogen (C_2N_2) and hydrogen cyanide (HCN). At high temperatures carbon unites with nitrogen to form the colorless, *very poisonous* gas cyanogen (C_2N_2). With hydrogen and nitrogen it forms hydrogen cyanide (HCN). This is a colorless liquid boiling at 26° . It has a peculiar odor suggesting peach kernels and is *extremely poisonous* either when its vapor is inhaled or when the liquid is taken internally. It is soluble in water in all proportions, forming the solution called *hydrocyanic acid* or very often *prussic acid*. It is a very weak acid. Its salts are called *cyanides* and, like the acid

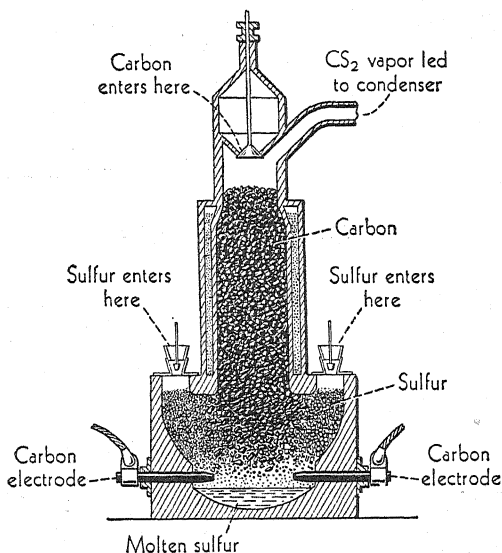
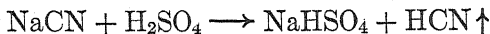


FIG. 273. *The Manufacture of Carbon Disulfide*

Heat is generated by an electric current, as shown in the figure. The sulfur is vaporized and, passing up through the hot carbon, unites with it to form the vapor of carbon disulfide. The vapor is liquefied by being passed through condensers

itself, are very poisonous. Sodium cyanide (NaCN) and potassium cyanide (KCN) are white solids. Their solutions readily dissolve gold (in the presence of oxygen) and are used in gold metallurgy and in electroplating.

Since hydrogen cyanide is very volatile, it is easily liberated from the cyanides by the action of sulfuric acid, and this is the usual method for preparing it:



Because of its poisonous properties hydrogen cyanide is used to destroy insects, especially those that infest citrus trees. It is sometimes used for ridding houses of moths and other insect pests. Because of its very poisonous character, *it should never be used in houses except by an experienced person who knows how to avoid all danger from its use.*

Questions

1. Titanium is apparently more abundant in the earth's crust than carbon. Why do we usually think of carbon as more abundant?

2. Davy found that CO_2 is the sole product of combustion of diamond. Does this prove that diamond is pure carbon?

3. If chemists were to learn how to make diamonds of jewel size, what would be some of the results of this discovery?

4. Both carbon and carbon dioxide pass directly from the solid state into the gaseous state. Why is it possible to liquefy carbon dioxide but not carbon?

5. Write the equation $\text{Fe}_2\text{O}_3 + 3 \text{C} \longrightarrow 2 \text{Fe} + 3 \text{CO}$ in the form of equations showing the transfer of electrons.

6. How many ways can you mention in which carbon monoxide is formed?

7. KCN can be easily changed into the salt KNCO . What should be the name of the salt?

8. The carbonates and sulfites have similar formulas and similar solubilities. In what other respects are they similar?

9. How should you expect calcium sulfide to react with carbon disulfide?

10. Given the elements carbon, oxygen, chlorine, nitrogen, and hydrogen, how could you prepare urea?

Problems

1. On analysis a compound gave the following results: carbon, 15.8 per cent; sulfur, 42.1 per cent; nitrogen, 36.8 per cent; hydrogen, 5.3 per cent. (a) Calculate the simplest formula for the compound. (b) Nineteen grams of the compound dissolved in 1 l of water lowered the freezing point of the water 0.4675° . What is the molecular weight of the compound?
2. What volume of carbon monoxide will be required for the synthesis of 30 g of urea by the use of carbonyl chloride?
3. What volume of carbon dioxide (standard) can be produced from 100 g of carbon?
4. What volume of carbon dioxide (standard) can be obtained by heating gently 200 g of $\text{Ca}(\text{HCO}_3)_2$?

Reading References

- CLARKE. *Marvels of Modern Chemistry*. Chapter XXIII tells of carbon in its various forms.
- FOSTER. *Romance of Chemistry*. Chapter XXI is entitled "Carbon, Producer of Energy."
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- GERVASI. "Flash," *Colliers Weekly*, February 24, 1940. The story of the recent discovery of the large Vargas diamond in Brazil.
- LITTLE. "The Romance of Carbon," *Industrial and Engineering Chemistry*, Vol. XVIII, pp. 444-451.
- RIEGL. *Industrial Chemistry*. Pages 292-295 tell of Carborundum. Pages 545, 546 tell of carbon black and lampblack.
- "Darkness by the Tank Car," *Journal of Chemical Education*, Vol. XIII, p. 45. Tells of carbon black (abstract).
- Both the *Encyclopaedia Britannica* and the *World Book Encyclopedia* contain excellent articles on diamonds. Many illustrations.
- The magazine *Fortune* contains two good articles on diamonds: Vol. XI, No. 5, p. 66, and No. 6, p. 96.
- Consult the *Minerals Yearbook* for information concerning coal, coke, and carbon black.

CHAPTER 26

Hydrocarbons; Petroleum

Organic chemistry. The compounds of carbon are probably more numerous than the known ones of all other elements combined; but just how many have been described no one has taken the trouble to find out, and new ones are being added to the number daily. Ten years ago it was estimated that there were over 200,000. Holmyard, in his text on organic chemistry, states that at least 500,000 are known. Certainly the number is constantly increasing through the discovery and preparation of new compounds, and a conservative estimate would give the present number as 350,000.

The great number of these compounds and their peculiarities of structure make it desirable to set them all apart as a special branch of chemistry. This branch is called *organic* chemistry, as distinguished from mineral, or *inorganic*, chemistry. *Organic chemistry is the chemistry of carbon compounds.* The great majority of carbon compounds are covalent in character except as their molecules contain substituting acid or basic groups.

A few of the simple compounds of carbon have been described in the preceding chapter. A limited number of more typical organic compounds must be described in the chapters that follow if the student is to have any knowledge of many familiar substances.

Historical. The origin of the term *organic chemistry* dates back to an early period, when it included those compounds of carbon found exclusively in living organisms. It was supposed that these compounds could be formed only through the influence of the living, or vital, force of the organisms, and that it would be impossible to prepare them in the laboratory by synthetic methods. In 1828 the German chemist Wöhler, in the course of some experiments, chanced to prepare a white crystalline compound which, much to his surprise, proved to be *urea*, a typical organic compound.

It was true that in preparing urea Wöhler had used compounds obtained indirectly from animal matter; but some chemists thought these compounds could hardly have retained any vital quality. They began to question the idea that vital force is essential to the formation of all organic compounds. It was not long before other compounds found in living organisms were synthesized in the laboratory from purely inorganic material, and the old belief concerning the formation of these compounds was gradually abandoned. The term *organic chemistry* was retained as con-

venient for designating the chemistry of all carbon compounds. This includes the study of most of the compounds found in living organisms, not because they are found in these organisms, but because they contain carbon.

The hydrocarbons. With hydrogen alone carbon forms many thousand different compounds, called *hydrocarbons*. A *hydrocarbon* is a compound consisting of carbon and hydrogen only. Under ordinary conditions some of the hydrocarbons are gases, others are liquids, and still others are solids. Many of them are compounds of the greatest importance, as may be inferred from the fact that mixtures of certain ones constitute such valuable substances as natural gas, gasoline, kerosene, lubricating oils, vaseline, and paraffin, while others serve as the raw material from which are prepared many of our most valuable dyes, medicinal agents, and explosives.

Classes of hydrocarbons. Since there are so many hydrocarbons, it is possible, in an introductory course in chemistry, to mention only a few of the most important ones. To simplify their study it is convenient to arrange them in groups, or *series*, one of the most important of which is the *methane series*.

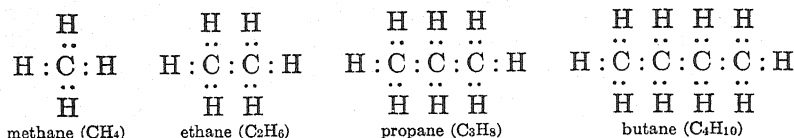
Methane series of hydrocarbons. The members of this series are often called the *paraffin hydrocarbons*, since ordinary paraffin is a mixture of some of the solid ones. In the table below are given the names, formulas, and boiling points of some of these compounds, arranged according to the number of carbon atoms present. Only the first eight members of the series are given; others are known, up to those containing nearly 100 carbon atoms.

NAME AND FORMULA	BOILING POINT	NAME AND FORMULA	BOILING POINT
Methane (CH ₄)	- 161.4°	Pentane (C ₅ H ₁₂)	+ 36.2°
Ethane (C ₂ H ₆)	- 88.3°	Hexane (C ₆ H ₁₄)	+ 69.0°
Propane (C ₃ H ₈)	- 44.5°	Heptane (C ₇ H ₁₆)	+ 98.4°
Butane (C ₄ H ₁₀)	+ 0.6°	Octane (C ₈ H ₁₈)	+ 124.6°

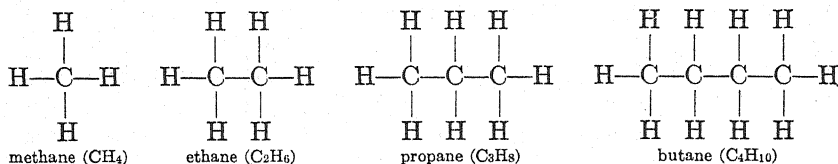
General formula, C_nH_{2n+2} (in which "n" is the number of carbon atoms)

A study of the table will show that *each member of the series differs from the one preceding it by the group of atoms CH₂*. Such a series of compounds is called a *homologous series*. In general it may be stated that the members of a homologous series are similar in their chemical conduct and show a regular gradation in some of their physical properties. For example, the boiling points of the compounds named gradually increase with each added CH₂ group.

Structural formulas of the hydrocarbons of the methane series. If we represent the valence electrons by dots, the formulas of the first four members of the methane series are as follows :



For the sake of simplicity, we often represent a pair of shared electrons by a dash, in which case the formulas become the following :



We often go a step farther and write semistructural formulas as follows :



Such formulas simply show the groups, or radicals, present, and the way they are combined to form the molecule. The carbon atoms in these formulas are represented as combined together, one after another, and so forming gradually longer molecules; indeed, they might be compared to the links that make up a chain. It is this property of carbon atoms to combine covalently one with another that makes possible the existence of so large a number of hydrocarbons, as well as other carbon compounds.

Properties and chemical conduct of the hydrocarbons. The hydrocarbons of the methane series are all colorless compounds. The first four, namely, methane, ethane, propane, and butane, are gases under ordinary conditions of temperature and pressure. Those containing from 5 to 16 carbon atoms are liquids, the boiling points of which increase with the number of carbon atoms present; those containing more than 16 carbon atoms are solids. The hydrocarbons are insoluble in water and are not readily acted upon by other compounds; even strong acids and bases have little or no effect upon them. All of them, however, are combustible, the lower members of the series very readily so. When they burn, the carbon and the hydrogen unite with oxygen and form carbon dioxide and water.

Petroleum. The great natural source of the methane hydrocarbons is *petroleum*. This is a dark-colored liquid found underground in certain localities. It varies somewhat in composition according

to the locality; in general it is composed of liquid hydrocarbons in which are dissolved both gaseous and solid ones, but not all of these belong to the methane series. In order to obtain the petroleum, wells are sunk into the oil-bearing strata, which vary in depth from a few feet to over 2 miles. Sometimes petroleum is under such pressure that it will flow to the surface of the earth in large volumes when the well reaches the petroleum; more often it must be pumped to the surface. It is then stored in tanks until needed for refining.

Many useful products are obtained from petroleum; among them are the various kinds of *naphthas*, *kerosene*, *lubricating oils*, *vaseline*, and *paraffin*. These products are not single compounds but are mixtures of hydrocarbons boiling between certain limits. Since these oils are derived from petroleum, which is obtained from the earth, they are often termed *mineral oils*, to distinguish them from oils derived from animal and vegetable sources. The word *petroleum* is derived from two Latin words signifying "rock oil."

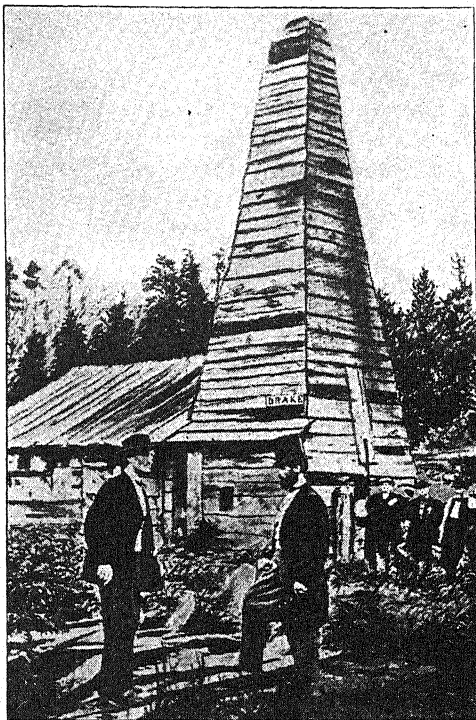


FIG. 274. *The First Oil Well in the United States*

This well was drilled by Colonel Drake at Titusville, Pennsylvania, in 1859. The well was 70 ft deep and furnished about fifteen barrels daily

Historical. The petroleum industry was first developed in the United States. For more than a century this liquid had been found oozing from the ground in various localities in Pennsylvania and New York. It was first placed on the market in 1849 by a Pittsburgh druggist, who sold it at fifty cents for a half-pint bottle as "A Natural Remedy! Celebrated for its wonderful curative powers." A few years later, experience showed that the oil readily burned and that it had many possible uses. The first oil well was sunk at Titusville, Pennsylvania, in 1859 (Fig. 274).

Production of petroleum. The annual world production of petroleum varies from year to year, but in general it amounts to about 1,500,000,000 barrels of 42 gal each. Of this amount the United States produces more than half. The chief oil-producing states are Texas, California, and Oklahoma. The principal foreign oil-producing countries are Russia, Mexico, and Rumania.

The refining of petroleum. The composition of petroleum varies with the locality in which it is found. In general it is made up of various hydrocarbons mixed with certain impurities, such as compounds of sulfur. Before it is suitable for most uses, the oil must be refined. This process consists in separating the oil into fractions, each adapted to certain definite uses, and in removing the impurities. The steps involved in refining the crude oil are as follows:

1. **Fractional distillation.** The crude oil is first subjected to fractional distillation. Various kinds of stills are used, but the principle involved is shown in Fig. 275. The products distilling between certain temperatures are

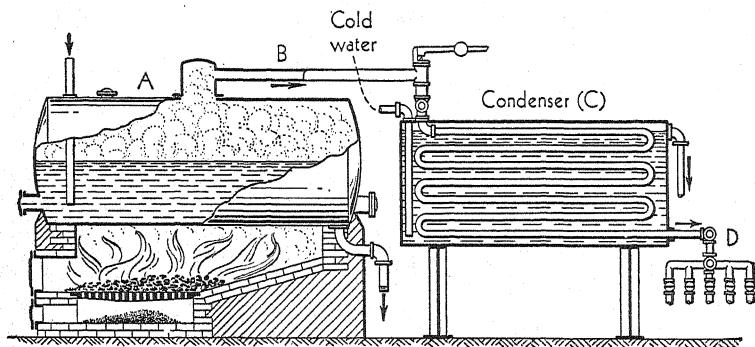


FIG. 275. Diagram of a Simple Apparatus, Illustrating the Principle Involved in the Distillation of Petroleum

The crude oil is run into the large still A and heated. The vapors pass off through B and are condensed in C. The resulting liquids are drawn off through D

collected separately, and different names are given to the fractions. In general the fraction that distills below about 200° is known as *naphtha*, from which *gasoline* is obtained by further distillation; that distilling between 200° and 300° is called *refined-oil distillate*, and is the source of *kerosene*. Next is obtained a fraction known as *fuel oil* (or some similar term), used as a fuel for heating our homes and also in certain types of engines. The final distillation product is the *paraffin distillate*, from which are obtained the various grades of lubricating oil and paraffin. When this distillate is cooled to 0° , the paraffin present crystallizes and is removed by filter presses.

2. Purification of the distillates. The different distillates obtained by fractional distillation are run into large tanks and agitated with sulfuric acid, which combines with most of the objectionable compounds present. After the agitation the acid (containing the impurities) settles to the bottom of the tanks and is drawn off. The remaining oils are then washed with water and finally with a solution of sodium hydroxide to remove all traces of acid. If sulfur compounds are present, they must be removed from the distillates used as a source of naphtha and kerosene by additional processes.

3. Redistillation. Finally the different products, after treatment with the acid and alkali, are distilled once more. The lubricating oils are often filtered through a grade of fine clay known as fuller's earth.

The naphthas. Various grades of naphthas are produced and used for different purposes; their great use is as *gasoline* for fuel in internal-combustion motors. *Benzine* is a grade of naphtha used in the paint industry and as a solvent.

Methods for obtaining additional supplies of gasoline. In the days of the kerosene lamp, kerosene was the most important of the products obtained from petroleum. With the advent of the gasoline engine, gasoline became the most valuable of the products, so that every effort was made to increase its yield from petroleum, as well as to find new sources for this product. The most important of these are as follows:

1. The cracking of oils. It was discovered that the yield of gasoline obtained from any sample of oil could be greatly increased by carrying on the distillation under conditions that tend to decompose the larger molecules, which make up the higher-boiling liquids, into the smaller molecules, which constitute gasoline and similar products. This process is known as the *cracking of oils*. It is accomplished by a number of different methods, such as carrying on the distillation under high pressure or passing the hot vapors over certain catalysts. In this way the yield of gasoline from petroleum can often be doubled or even trebled.

2. Casinghead gasoline. Ordinary natural gas, largely used as a fuel, is chiefly methane (CH_4); but the natural gas from many wells is saturated with the vapors of low-boiling hydrocarbons, such as hexane and heptane (p. 467). These vapors are separated from the gas by various methods and yield a high grade of gasoline called *casinghead gasoline*.

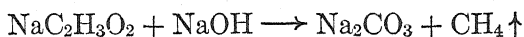
3. The hydrogenation of coal. Another method, developed by the German chemist Bergius (for which discovery he was awarded the Nobel prize), consists in treating finely powdered coal, dispersed in an oil, with hydrogen under high pressure, in contact with a suitable catalyst, and at a temperature around 500° . Under these conditions there are formed various useful products, including lubricating oils, kerosene, and gasoline. The process promises much for the future when the natural supplies of petroleum may be exhausted.

Oil from shales. In Colorado and some other Western states there are enormous deposits of shales (a fossil rock). When these are heated, complicated reactions occur that result in the formation of a number of valuable

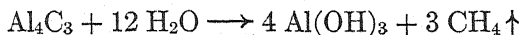
products, including a petroleum-like liquid. While these shales are not utilized at present in America, they may become valuable when our deposits of petroleum become exhausted.

Methane (marsh gas) (CH_4). This hydrocarbon constitutes from 50 to 90 per cent of natural gas. It is formed in marshes by the decay of vegetable matter under water, and bubbles of the gas are often seen to rise when the dead leaves on the bottom of pools are stirred. It also collects in mines, and, when mixed with air, is called *fire damp* by the miners because of its great inflammability, *damp* being an obsolete word for vapor or for a gas. It is formed when organic matter, such as coal or wood, is heated in closed vessels; it is therefore a principal constituent of ordinary coal gas. It is also formed when hydrogen is passed over a mixture of powdered carbon and nickel heated to 300° .

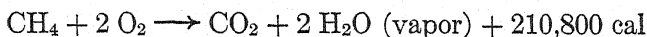
Methane is prepared in the laboratory by heating sodium acetate with sodium hydroxide (or with a mixture of sodium and calcium hydroxides known as soda lime):



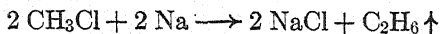
It can also be prepared by the action of water on aluminum carbide:



Methane is a colorless, odorless gas 0.55 times as heavy as air, and is almost insoluble in water. It burns with a pale-blue flame and evolves much heat, as shown in the equation



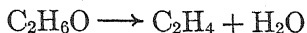
Ethane (C_2H_6). Ethane is similar to methane in its properties. It can be prepared from methane by first displacing an atom of hydrogen by one of chlorine and then treating the resulting compound with sodium:



Hydrocarbons belonging to other series. The hydrocarbons so far described all belong to the methane series. A great many belonging to other series are known. Two of these, namely, *ethylene* and *acetylene*, are of great importance and merit special description.

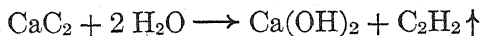
Ethylene (C_2H_4). Ethylene is a colorless, inflammable gas. Coal gas contains a small percentage of it. It can be prepared by removing the elements of water from ordinary alcohol (ethyl alcohol, $\text{C}_2\text{H}_6\text{O}$), either by heating the alcohol with sulfuric acid or by passing its

vapor through a tube filled with a porous aluminum silicate heated to about 500°:

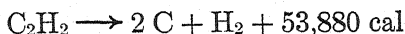


Ethylene is used (1) as a source of heat, (2) as an agent for speeding up the ripening of citrus fruits, (3) in the manufacture of ethylene dibromide, and (4) as an anesthetic in surgical operations. Although ethylene has been known since 1795, it was not until 1923 that its anesthetic property was discovered. This happened in an interesting way. A Chicago florist found that carnations stored in his greenhouse soon withered. Dr. Crocker, a botanist of the University of Chicago, was called in to find the cause of this and soon located it in the coal gas escaping from one of the pipes. Further experiments convinced him that it was the ethylene in the coal gas that was responsible for the trouble. Subsequently the effect of the ethylene on rats was tried. The rats soon toppled over, as did the carnations, and were left for dead. Much to the astonishment of the experimenters the rats were soon found to be running around again as lively as ever. This suggested the possible use of ethylene as an anesthetic and led to extensive experiments which resulted in placing it on the list of our important anesthetics.

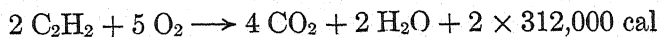
Acetylene (C_2H_2). This is a colorless gas, 0.92 times as heavy as air, which can be made by the direct combination of carbon and hydrogen at very high temperatures. It also results when certain hydrocarbons are burned in a limited supply of air, so that the combustion is incomplete. In this way it is formed when the flame of a Bunsen burner "strikes back," that is, when the flame burns at the bottom of the tube. The easiest as well as the most economical method for its preparation consists in the action of water upon calcium carbide:



Acetylene, when pure, has a faint, rather pleasant odor. As ordinarily prepared, however, it has a disagreeable odor due to impurities. It can be condensed to a liquid boiling at -83.6° . It is an endothermic compound, and in the formation of a gram-molecular weight of the gas 53,880 cal are absorbed. When the compound is decomposed, this same quantity of heat is evolved:



Acetylene, with the proper admixture of air, burns with a brilliant white light. The flame is very hot because to the heat of combustion of the carbon and hydrogen present there is added the heat of decomposition of the acetylene undergoing combustion:



Preparation and combustion of acetylene. The gas can be prepared in a generator such as is shown in Fig. 276. The inner tube *A* contains lumps of calcium carbide, while the outer one is filled with water. As long as the stopcock *B* is closed the water cannot rise in the inner tube. When the stopcock is open, the water rises and, coming into contact with the carbide, generates acetylene. The gas escapes through the stopcock and may be lighted as it issues from the burner.

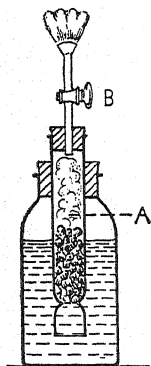
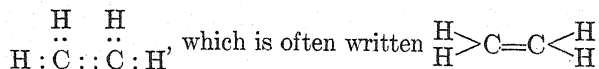


FIG. 276. The Generation and Combustion of Acetylene

Acetylene is very explosive when subjected to pressure. It has been found, however, that the gas can be compressed with safety by forcing it at low temperatures into metal cylinders completely filled with some porous material which has been partially saturated with certain liquids, especially the compound called acetone. These liquids absorb large volumes of the gas, and under such conditions it is not explosive. Stored in this way the gas is now a commercial article.

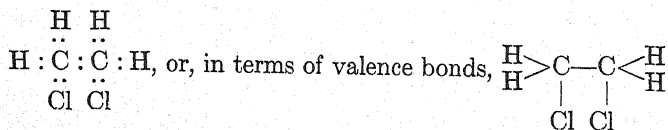
Uses of acetylene. Formerly acetylene was largely used as an illuminant, but the electric light has almost entirely taken its place. The chief use of the gas at the present time is in the cutting and welding of metals (see oxyacetylene blowpipe).

Constitution of ethylene and acetylene. Hydrocarbons may be classified into two groups, the *saturated* and the *unsaturated*. The saturated hydrocarbons, which include those belonging to the methane series, will not combine directly with any other element or group of elements. Ethylene and acetylene are unsaturated and combine directly with certain elements, such as chlorine and bromine. Thus ethylene combines with two atoms of chlorine, forming $C_2H_4Cl_2$. If the electrons are represented by dots, the formula of ethylene is as follows:



and the carbon atoms are said to be joined by a *double bond*. The latter formula is the one generally used by chemists.

When ethylene is brought in contact with chlorine, one of the double bonds "opens" and the chlorine combines directly with the carbon atoms, giving the compound



In acetylene, the two carbon atoms are joined by a *triple bond*, as shown in the structural formula $\text{H}-\text{C}\equiv\text{C}-\text{H}$. In contact with chlorine under proper conditions, one of the bonds uniting the two carbon atoms "opens," adding two chlorine atoms and giving the compound $\text{C}_2\text{H}_2\text{Cl}_2$; or two of the bonds may "open," adding four atoms of chlorine and forming the compound $\text{C}_2\text{H}_2\text{Cl}_4$.

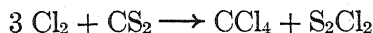
Substitution products of the hydrocarbons.

We have seen that the hydrocarbons are readily combustible; they are all alike in another respect, namely, that their hydrogen can be displaced by certain elements, especially by the halogens. For example, 1, 2, 3, or 4 hydrogen atoms of methane can be displaced by chlorine, forming the compounds CH_3Cl , CH_2Cl_2 , CHCl_3 , CCl_4 respectively. Such compounds are called *substitution products*. Many of these compounds are of the greatest importance. Among them are the following substitution products of methane:

1. **Chloroform (CHCl_3)**. This is a well-known compound used as an anesthetic in surgery. It is a colorless, heavy liquid boiling at 61° , and is a good solvent for many organic compounds.

2. **Iodoform (CHI_3)**. Iodoform is a yellow crystalline solid once used as an antiseptic in the treatment of wounds.

3. **Carbon tetrachloride (CCl_4)**. This compound is a heavy, colorless liquid boiling at 76.8° . It is prepared by the action of chlorine on carbon disulfide:



Like chloroform and benzine it is a good solvent for many organic compounds, such as oils and fats, and is sometimes used for this purpose in dry cleaning. It is a very effective specific for the treatment of hookworm disease. Its main use is as a fire-extinguisher.

Carbon tetrachloride as a fire-extinguisher. The liquid used in these extinguishers is known by the trade name Pyrene and consists chiefly of carbon tetrachloride. The liquid is contained in a small metal cylinder that can be easily grasped by the hand (Fig. 277). The cylinder is fitted with a sort of piston for forcing the liquid out in case of fire. The liquid is non-

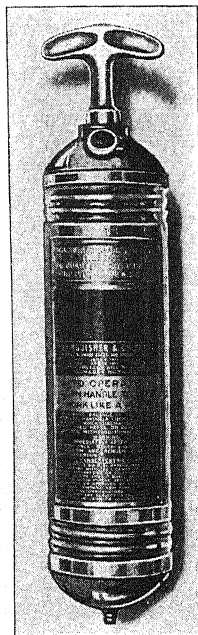


FIG. 277. A Fire-Extinguisher in Which Carbon Tetrachloride Is the Extinguishing Agent

combustible and is quite volatile. When sprayed onto a fire it volatilizes, and its heavy vapor surrounds the burning body and prevents the oxygen of the air from coming in contact with it.

4. *Dichlorodifluoromethane* (CCl_2F_2). This is an easily condensed gas (boiling point, -29.8°). It is derived from methane by replacing

two of the hydrogen atoms in methane by fluorine and two by chlorine. Although it is a gas containing both fluorine and chlorine, *it is nonpoisonous*. It is a colorless and practically odorless compound, and it, as well as related derivatives of ethane, is largely used as a refrigerant in mechanical household refrigerators (p. 124).

Rubber. Pure rubber, or *caoutchouc*, is a hydrocarbon, and so may be studied in connection with other hydrocarbons. Like steel and glass, rubber has become an article of absolutely prime importance in our modern life. Many millions of pounds are used annually in the United States, by far the greater percentage of which goes into the motorcar industry.



Galloway

FIG. 278. *Tapping a Tree on a Rubber Plantation*

Rubber is a product of many tropical trees, of which the most valuable species grows wild in the Upper Amazon region of South America, and is now cultivated in tropical regions such as Java, Sumatra, Ceylon, Liberia, and the Malay States. At present by far the largest percentage of the world's output comes from rubber plantations. These have increased from practically no acreage in 1900 to many millions of acres at present. The rubber is obtained from the trees by "tapping" (cutting through the bark (Fig. 278)). A fluid runs from the incisions down the trees and is collected in

buckets. This fluid, which is called *latex*, and which resembles milk in appearance, is an emulsion consisting mainly of minute rubber particles dispersed in water, and contains from 25 to 35 per cent of rubber. Geer, in his book *The Reign of Rubber*, states that the number of these particles is so great that if those present in 1 gal of latex were placed side by side, they would make a tiny rubber thread 372 miles long. The latex contains a small percentage of nitrogenous matter, which acts as a protecting colloid (p. 443) and prevents the coalescence of the rubber particles. A little acetic acid added to the latex destroys the action of the protecting colloid, so that the rubber at once separates and collects in the form of a soft white dough (Fig. 279).

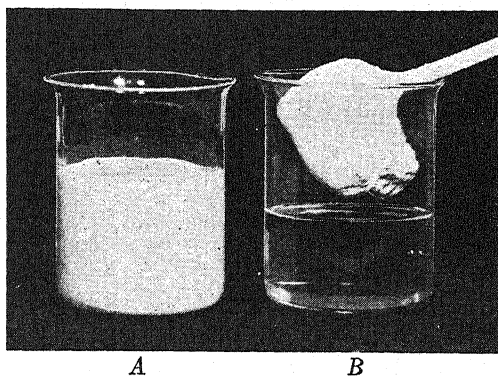


FIG. 279. *The Coagulation of Rubber Latex by Acetic Acid*

A shows the latex, and B the coagulated rubber

Not only is all the rubber we use imported, but large quantities of the latex also are imported. The latex is well adapted to many uses, especially in the manufacture of certain kinds of paper and artificial leather.

Composition of rubber. Pure, natural rubber is a polymer of the unsaturated hydrocarbon *isoprene*; in other words, it consists of a large number (about 1000) of the molecules of isoprene united to form a long, threadlike molecule of rubber. Isoprene has the formula

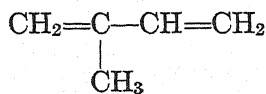


Fig. 280 shows how three of the isoprene molecules are united in the rubber molecule. Imagine about 1000 of the isoprene molecules to be united in the same way, and you will have a picture of the rubber molecule.

Vulcanizing rubber. An article made of raw rubber would be of little value, since it would become hard and brittle in cold weather and very soft and sticky in warm weather. In 1839 Charles Goodyear of New Haven, Connecticut, found that if rubber is heated with a

small percentage of sulfur under proper conditions, these objectionable qualities disappear. This process is called *vulcanization*. Sulfur monochloride (S_2Cl_2) is sometimes used as a means of adding the sulfur. The time required for vulcanization can be reduced to a few minutes by using, with the sulfur, a small percentage of certain organic compounds called *accelerators*, which act as catalysts to increase the speed of the reaction. Just how the sulfur reacts is not definitely known.

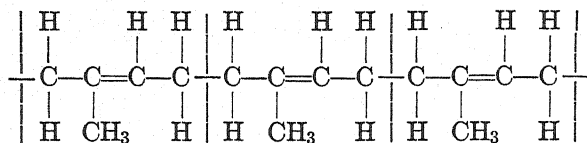
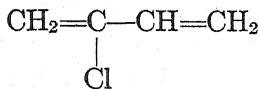


FIG. 280. Portion of a Rubber Molecule, Showing Isoprene Units

Rubber mixtures. Various other compounds, such as carbon black, zinc oxide, and antimony sulfide, are also added to rubber which is to be vulcanized. These give the rubber greater strength or a desired color. The improvement in the service-life of automobile tires from the average 5000 miles of a few years ago to about 25,000 miles today is due largely to the addition of the substances mentioned above or of similar ones, as well as to the improved fabric of the casings.

Chloroprene rubber, or neoprene. The work of Nieuwland and Carothers and their associates has led to the synthetic preparation of a new rubber, called *neoprene*, with acetylene as the source material. This new rubber is a polymer of chloroprene,



which is exactly like isoprene except for the substitution of a chlorine atom for the methyl radical (CH_3). Neoprene is too expensive to use in the manufacture of tires (although it makes good ones), but it possesses properties that make it much more desirable than natural rubber for certain other purposes. For example, it is resistant to sunlight, oxygen, acids, oils, and greases. It is used for lining all sorts of tanks, as well as for hundreds of other special purposes.

There has been a great amount of development, particularly in Europe, of an artificial rubber called *buna*, which is made from butadiene, $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$. Since butadiene may be obtained

in large quantities from the cracking of petroleum, the next few years will probably witness the manufacture of buna rubber in large quantity.

Questions

1. Why should there have been a belief that a vital force is necessary in the formation of organic compounds?
2. What is the meaning of the word *paraffin*?
3. Why should there not be as many compounds of sulfur as of carbon?
4. Why must sulfur be removed from the various petroleum distillates?
5. In purifying petroleum distillates, how can an oil be "washed with water"?
6. On what grounds can a dealer in gasoline legitimately claim that his product is superior to some other brand?
7. Should it be possible to build up molecules suitable for gasoline from smaller ones, such as those of methane or ethane?
8. What should you expect to be formed by heating sodium propionate ($\text{NaC}_3\text{H}_5\text{O}_2$) with sodium hydroxide?
9. What is the electronic formula for $\text{C}_2\text{H}_2\text{Cl}_4$?
10. (a) What gives the red color to many rubber articles? (b) What gives the black color?

Problems

1. By simple inspection of the equation answer the following: (a) How many liters of acetylene gas can be obtained from 1 g-mol. wt of calcium carbide; (b) what volume of oxygen will be required for its combustion; (c) what volume of carbon dioxide will be produced?
2. What volume of dry air will be required for the combustion of 50 l of ethane?
3. If methane is burned in oxygen and the water vapor formed is condensed to water at 20° instead of remaining as vapor, as in the equation on page 472, what is the gram-molecular heat of the reaction?
4. What volume of marsh gas must be burned to give heat equal to the heat of combustion of the acetylene produced from 1 g-mol. wt of calcium carbide?
5. If sodium acetate is used as a source of methane and calcium carbide as a source of acetylene, what weight of the former will be required to produce a volume of methane equal to the acetylene produced from 32 g of calcium carbide?

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- The magazine *Fortune*, Vol. XVIII, No. 1, p. 50, contains an article entitled "The Deepest Oil Well"; Vol. XIV, No. 5, p. 99, contains an article on tires.
- Consult the Minerals Yearbook for information concerning the production of petroleum.

CHAPTER 27

Flames; Fuel Gases; Explosions

Visible combustion. When combustion proceeds rapidly, the heat liberated is readily perceived, and the reaction is accompanied by light (p. 95). The products of combustion may be solids, as in the case of metals such as iron; or they may be easily condensed vapors, as in the case of hydrogen; or they may be gases, as with carbon and sulfur. If the burning substance is a solid and remains so during combustion, it may become incandescent but there is no flame. This is the case with the combustion of pure carbon and many of the metals. When both of the substances involved in the combustion are gases, the bounding surface between the two presents the appearance known as a flame; and this flame is usually, though not always, distinctly luminous.

The fact that a flame often accompanies the combustion of solids (coal, wood, or a candle) or of liquids (oils) does not contradict the statements just made; for in such cases the heat of combustion produces vapors from the solid or liquid, and these in turn burn with a flame. If one end of a slender glass tube is held in the base of a candle flame, as indicated in Fig. 281, a flame is formed when a lighted match is held at the other end, showing that gases are produced from the candle which can be drawn off and ignited separately. The blue flame over a bed of coals is the flame of burning carbon monoxide formed by the partial combustion of the carbon.

Fuel gases. Before considering the structure of flames it will be of advantage to have before us the general chemical characteristics of the gases whose combustion gives rise to the most familiar examples of flames. A number of varieties of gases are now employed as sources of heat, light, and power.

1. **Coal gas.** It has been known for several centuries that when soft, or bituminous, coal is heated out of contact with air, combustible gases are formed; indeed, gas obtained in this way was

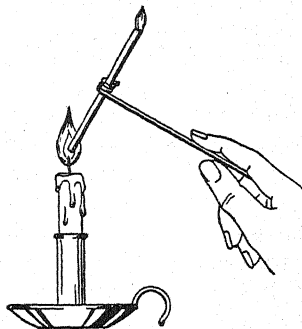


FIG. 281. Experiment to Show that the Solid Material of the Candle Vaporizes before Burning

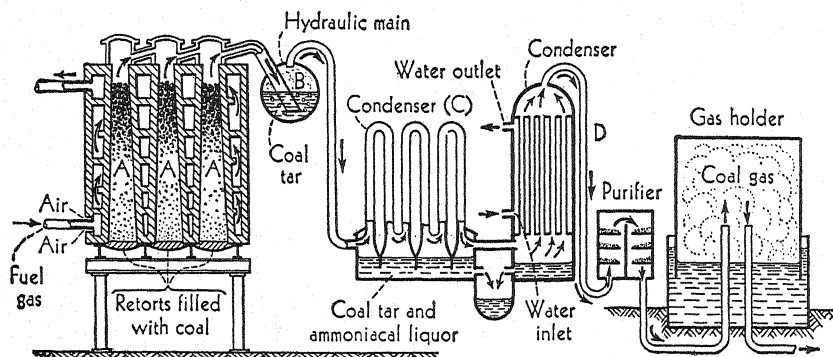


FIG. 282. Diagram Illustrating the Manufacture of Coal Gas

used for street-lighting in London, England, as far back as 1812 and in Baltimore, Maryland, in 1817.

The manufacture of coal gas. The manufacture of coal gas is represented in a diagrammatic way in Fig. 282. The coal is introduced into rows of closed retorts, A, A, A, and heated. A delivery pipe leads from the top of each of the retorts into a large pipe B (known as the *hydraulic main*). The heat brings about complex changes in the coal which result in the formation of a large number of compounds. Those that are volatile escape through the delivery pipe into the hydraulic main. At the lower temperature of the main, portions of those products that are solid or liquid at ordinary temperatures condense in the form of a dark liquid called *coal tar*. The gases pass on into the *condenser C*, in which they are cooled to such an extent that any tar carried with them is largely deposited. Along with the tar there is condensed a liquid (chiefly water) containing ammonia in solution and known as *ammoniacal liquor*. The gas is then led into a large iron drum D, fitted with copper tubes, through which the gas passes. The tubes are kept cool by running water, and further condensation of vapors takes place in the tubes. From the drum D the gas passes into the purifier, where it comes into contact with lime or iron oxide, which removes any sulfur compounds still remaining. The gas then enters the large gas holder, from which it is distributed to consumers.

The great bulk of the carbon remains in the retort as *coke* and as *retort carbon*. The yield of gas, tar, and soluble materials depends upon many factors, such as the composition of the coal, the temperature employed, and the rate of heating. One ton of good gas coal yields approximately 10,000 cu ft of gas, 1400 lb of coke, 120 lb of tar, and 20 gal of ammoniacal liquor.

Not only is the ammonia obtained in the manufacture of the gas of great importance, but the *coal tar* is the source of many very useful substances, as will be explained later.

The by-product coke oven. It will be observed that coke is one of the products formed in the manufacture of coal gas. Coke is a very important product and is used in large quantities, especially in the reduction of metals, such as iron, from their ores. The quantity of coke obtained in the manufacture of coal gas has never been sufficient to meet the demand. Formerly all the additional coke required was prepared by coking the coal in ovens called *beehive ovens* because of their shape. This process is carried out as follows: The oven is nearly filled with coal, and the coal is set on fire. After the fire is well started the draft is shut off, and the heat liberated in the combustion of a portion of the coal converts the remainder of the coal into coke. In this process all the coal tar, coal gas, and ammonia are lost.

The growing demand for ammonia, as well as for the products obtained from coal tar, has led to the introduction of furnaces or ovens for coking coal which make it possible to save the coal tar, gas, and ammonia formed in the process. These ovens have almost entirely replaced the beehive ovens and are called *by-product coke ovens* because the tar, gas, and ammonia are the by-products, and the coke is the main product (Fig. 283).

In the manufacture of coal gas, stress is laid upon the yield of gas, while in the by-product oven it is placed upon the yield of coke. The difference in the results obtained is due mainly to the difference in the grade of coal selected, as well as in the heat treatment.

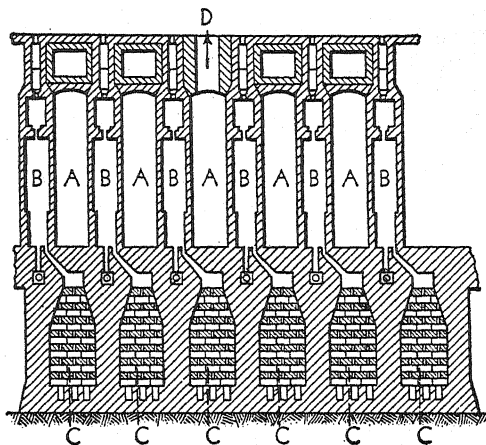
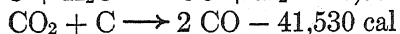
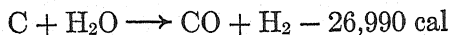


FIG. 283. Vertical Section of a Row of By-Product Coke Ovens

The ovens *A* are placed side by side, and separated from each other by the combustion chambers *B*. The ovens are made of silicious material and are narrow, so that the heat can penetrate the coal with which they are filled. The gas generated in the process may be used as the fuel; more often this is saved and a much cheaper gas is manufactured (producer gas) for coking the coal. A high temperature is secured by preheating the air used in combustion. This is done by having two sets of compartments *C*, loosely filled with bricks. First, the hot products of combustion are led from the heating chambers *B* through one set of the compartments *C*, until the bricks become very hot. The hot gases are then diverted through the second set of compartments, while the air required for combustion is led over the hot bricks into the heating chamber, where it meets the necessary supply of coal gas. By the time the bricks in the first set of compartments are cool, those in the second set have become heated and the flow of gases is interchanged. The gaseous products formed in the coking of the coal escape through the pipe *D* and are separated and purified much as in the process for making coal gas

2. Water gas. Water gas is essentially a mixture of carbon monoxide and hydrogen. It is manufactured by passing superheated steam over very hot anthracite or coke, the chief reactions being expressed in the following equations:



The industrial process is intermittent. The fuel is burned with a forced draft in a suitable furnace until it is very hot. The air is then shut off and the steam turned on until the temperature falls to about 1000° . The process is then reversed. The fall in temperature is rapid, partly owing to radiation and to the cooling occasioned by the steam, but largely because of the endothermic character of the reactions. The gas so formed contains the nitrogen which was in the furnace when the steam was admitted.

Water gas burns with a pale-blue, nonluminous flame. Among industrial fuel gases only acetylene gives a hotter flame. It is very poisonous and has no odor. To give it an odor and so make it safer for domestic uses, it is enriched with hydrocarbons. This is accomplished by passing the gas through a furnace filled with hot firebrick piled in the form of checkerwork, upon which crude petroleum is sprayed. The petroleum oils are decomposed (cracked) into simpler

gaseous compounds, the most important of which are methane, acetylene, and ethylene. Coal gas is sometimes enriched in a similar way by adding petroleum to the coal in the retorts.

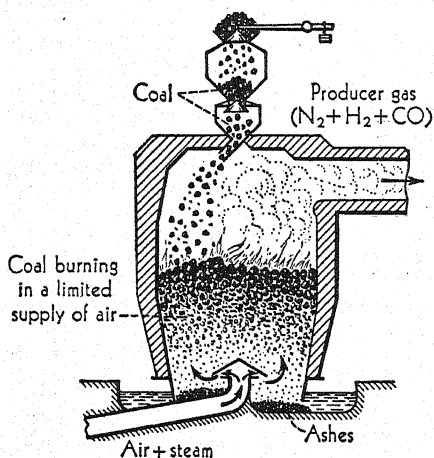


FIG. 284. Diagram Illustrating the Manufacture of Producer Gas

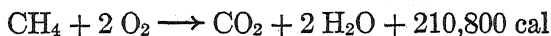
3. Producer gas. Producer gas is used in connection with many metallurgical furnace operations and also as a fuel for gas engines. It is made by burning coal in a mixture of air and steam under such conditions that the resulting products are largely carbon monoxide and hydrogen (Fig. 284). It also contains the nitrogen present in the air used, and this detracts

from its fuel value. It can, however, be made from coal of a poor quality, even from lignite; and as gas engines run well with this

gas, it furnishes the most economical method for utilizing low-grade coal for power. Producer gas is used not only as a fuel but also as a source of the nitrogen and hydrogen used in making ammonia by the Haber process (p. 379). When it is desired for this use, an excess of steam is added, and this converts the carbon monoxide into the dioxide, which is then removed by dissolving it in water.

4. *Natural gas.* Like petroleum, natural gas is obtained by boring wells into gas-bearing strata. It is usually associated with petroleum and is composed chiefly of methane, with small percentages of other hydrocarbons. The methane content averages about 80 per cent, although the gas from some fields contains as high as 90 per cent of methane. Nitrogen is generally present, but in very small quantities except in rare instances. Thus, the natural gas from the region of Fort Worth, Texas, contains as much as 38 per cent of nitrogen, while the methane content is about 50 per cent. It is interesting that natural gas rich in nitrogen usually contains about 1 per cent of helium.

Natural gas is an ideal fuel and is often conducted through pipes for hundreds of miles from the gas fields to cities. It burns with a flame of moderate luminosity but works well with a gas mantle. It has a high heat of combustion (much higher than that of coal gas), as shown in the following equation :



Comparative composition of gases. The figures in the table below are the results of analyses of average samples; but since each kind of gas varies considerably in composition, the values are to be taken as roughly approximate only. The nitrogen and traces of oxygen are derived from the air.

Average Percentage Composition of Gases by Volume

	NATURAL GAS	COAL GAS	WATER GAS	ENRICHED WATER GAS	PRODUCER GAS
H ₂		52.5	52.88	32.0	21.1
CH ₄	90.7	30.0	2.16	13.1	4.0
C ₂ H ₆	3.8	0.8		2.9	
C ₂ H ₄		2.0		9.8	
CO		6.8	36.80	29.8	19.8
CO ₂		1.7	3.47	4.8	6.8
N ₂	1.0	3.5	4.69	1.3	48.3
O ₂		0.6			
Other hydrocarbons . . .	4.5	2.1		6.3	

Relation of the two gases to the flame. The gas issuing from the burner is said to *undergo* combustion, while that one which constitutes the atmosphere about the flame is said to *support* combustion. This distinction is merely a matter of custom, since the relation of the two gases may be reversed without greatly altering the appearance of the flame.

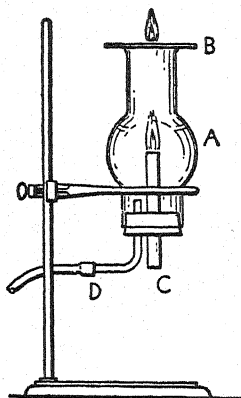


FIG. 285. *Burning Gas in Air and Air in Gas*

Apparatus. Fig. 285 illustrates a convenient apparatus for demonstrating this fact. A wide lamp chimney *A* is covered with a piece of asbestos board *B*, which has a hole in the center about as large as a dime. A straight tube *C* about 1 cm in diameter, and also a smaller tube *D* connected with the gas supply, pass through a cork at the bottom. If the hole in *B* is closed (by a piece of asbestos board) while gas is admitted through *D*, the excess gas escapes downward through *C*, where it may be lighted. The hole in *B* is now uncovered, and at once the flame ascends to the top of the tube *C*. This flame is produced by air drawn up through *C*, burning in an atmosphere of coal gas. Finally the excess of coal gas may be ignited at *B*, where it will burn in air. We now have two flames, one produced by gas burning in air and the other by air burning in gas.

Products of the combustion of ordinary fuels. Ordinary fuels, such as oil, wood, coal, and fuel gases, are largely made up of carbon and hydrogen or their compounds. The chief products of the combustion of such fuels are carbon dioxide and water. Associated with these are small amounts of other products, such as carbon monoxide and sulfur dioxide (if traces of sulfur compounds are present in the fuels).

The calorific value of fuels. The various materials used as fuels differ much in the heat which they give out when burned. While many other factors are concerned in the value of a fuel, the chief one is its heat of combustion. *The heat evolved by the combustion of one gram of a (solid or liquid) fuel is called its calorific value.* Sometimes the heat developed by 1 lb of a fuel is expressed in British thermal units (Btu) and called the calorific power. 1 Btu = the heat required to raise 1 lb of water $1^{\circ}\text{F} = 252\text{ cal}$. In large contracts the price paid for a fuel is, as a rule, based on its calorific value as well as on its adaptability to the desired use. The following table gives some average values for a few common fuels:

Calorific Values of Fuels

Wood (air-dried)	about 3800-4000 cal
Lignite (brown), 8% ash, 12% moisture	about 5400 cal
Bituminous coal (Pennsylvania), 35% volatile matter, 6% ash	about 8300 cal
Bituminous coal (Pocahontas), 18% volatile matter, 6% ash	about 8700 cal
Anthracite (Connellsville), 12% ash	about 7300 cal
Coke, 10% ash	about 7300 cal

Structure of a flame. The structure of a flame can be studied to the best advantage when the combustible gas issues from a round tube into an atmosphere of the gas supporting combustion (usually air), as is the case with an ordinary Bunsen burner. Under these conditions the flame is conical in outline (Fig. 286).

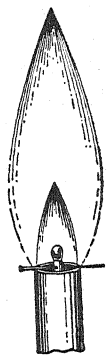


FIG. 286. A Simple Flame

Simple flames. When the chemical action taking place in the combustion is the mere union of two gases, as is true in the union of hydrogen or carbon monoxide with oxygen, or of hydrogen with chlorine, the structure of the flame is very simple. It consists of two superimposed cones of different altitudes. The inner one may be shown to be merely cold unchanged gas, and is therefore not a real part of the flame. A match head suspended in this region (Fig. 286) before lighting the gas is not ignited by the flame around it.

Complex flames. In the burning of hydrocarbons, as well as of many other gases, the flame is more complex, and as many as four distinct cones may be distinguished (Fig. 287). As we have seen, the innermost cone *A* is really not a part of the flame. If a Bunsen burner is employed, with the ring at the base turned to admit plenty of air, the second cone *B* is sharply defined and is bluish green in color. If the burner tube is wide, or too much air is admitted, the rate of combustion in this cone may exceed the rate of flow of the gas, and in that case the cone will travel down the tube and burn at the base ("strike back"). As the air is shut off, it will be seen that a luminous spot appears at the apex of this cone, which gradually takes the form of a cone *C*, quite covering cone *B* and brightly luminous over all its surface. Finally, if some object is held so as to intercept the light from this region, it will be seen that there is a fourth cone *D*, which is only faintly luminous.



FIG. 287. A Complex Flame

Cause of the cones. Since the gases which give rise to multiplication of cones during combustion are always chemical compounds, such as hydrocarbons, it would appear probable that the cones are due to successive chemical reactions taking place in different regions. Smithells devised a very simple method of separating the two principal cones and ascertaining the character of the combustion in each one. The essentials of his apparatus are shown in Fig. 288.

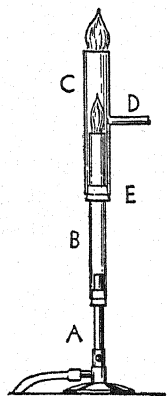


FIG. 288. *Method of Analysis of Flames*

Analysis of flames. The tube A (Fig. 288) of an ordinary Bunsen burner is extended in length by a glass tube B of slightly greater diameter. A wider tube C, of about 2 cm diameter and provided with a side tube D, surrounds this tube, to which it is connected by a cork E, through which the smaller tube slips easily. The wide tube C is slipped down until the ends of the two tubes are even; the gas is turned on and lighted at the top of these tubes, where it burns with a double cone. Air is admitted at the base of the burner until the inner cone is sharply defined and is bluish green in color. The outer tube is then pushed up, carrying the outer cone with it and leaving the inner one upon the rim of the smaller tube, as shown in the figure. The two cones are widely separated in this way, and the space between them becomes filled with the gases formed by the reactions taking place in the inner cone. These can be drawn off through the side tube D and analyzed.

Reactions in flames. In this way Smithells showed that in the inner cone the original hydrocarbons burn to form carbon monoxide and hydrogen, together with some unsaturated hydrocarbons, chiefly acetylene and ethylene. In the second, or luminous, cone the hydrogen and carbon monoxide are partly burned by the oxygen supply in the atmosphere, while the illuminants acetylene and ethylene are decomposed into carbon and hydrogen. The separated carbon becomes brilliantly incandescent and quickly undergoes combustion. The outer edge of the luminous flame marks its disappearance. The faint outside mantle is the region in which the combustion of carbon monoxide and hydrogen is completed.

Causes affecting luminosity. While the process just sketched accounts for the luminosity of flames in a general way, there are evidently a number of other factors which must be taken into account. Some flames, such as that of burning ammonia, are luminous, though there is no solid incandescent product formed during combustion. It is possible that, in the decomposition into elements

at a high temperature, endothermic compounds may give up some of their energy directly as light rather than as heat.

The temperature of the gases before combustion also affects luminosity. The nonluminous flame of a Bunsen burner becomes somewhat luminous when the tube of the burner is strongly heated. When the gas or the flame itself is cooled, the luminosity diminishes, as may be seen by bringing a large mass of cold metal, such as a flatiron, close to a luminous flame.

The concentration of the gases is also an important factor, for the luminosity becomes greater as the concentration is increased. Consequently pressure increases luminosity, as is shown by the fact that hydrogen under pressure burns in oxygen (also under pressure) with a luminous flame. On the other hand, dilution with an indifferent gas, especially if it is cold, greatly reduces luminosity.

The temperature of flames. The actual temperature which can be realized in an ordinary flame obviously depends upon many conditions, such as the composition of the gas, its pressure, initial temperature, rate of flow, and the method of supplying the air. Even in an ordinary Bunsen flame burning under favorable conditions it is very difficult to determine the maximum temperature attained. The actual region of great heat is very limited, as the burning zones are very thin. The temperatures in different parts of the flame are very different, and any object placed in the flame, for determining its temperature, cuts across many different regions and is unequally heated. Under exceptional conditions it has been found possible to melt a very fine platinum wire in a good Bunsen flame, showing that a temperature of 1755° is surely reached. The accompanying diagram (Fig. 289) gives a rough estimate of the probable temperature in various parts of a good nonluminous Bunsen flame.

Reducing and oxidizing flames. Since the region just below the luminous cone is very hot and contains the reducing gases hydrogen and carbon monoxide, a substance such as a metallic oxide, placed in this region, will undergo reduction, provided it can be reduced by such hot gases. This region is therefore called the reducing region, and a body heated in this way is said to be heated in the *reducing flame*. There are no reducing gases at the apex of the flame, but it is very hot and air is abundant; consequently a substance which is

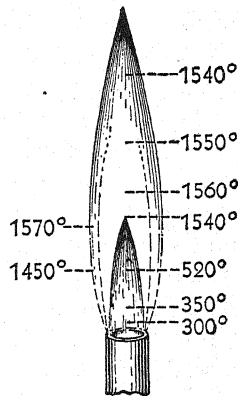
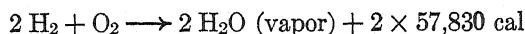


FIG. 289. *Temperature of Bunsen Flame*

rather readily oxidized will undergo oxidation if heated in this region. This is called the *oxidizing flame*.

Explosions. An explosion is caused by a sudden change in the pressure of gases following chemical reaction or by the sudden formation of gases from liquids or solids. The greater the pressure change, and the more rapidly it is produced, the more violent the explosion.

The equation of the reaction does not always supply the information necessary for predicting an explosion. Thus, when 2 volumes of hydrogen and 1 volume of oxygen are mixed and ignited, they form 2 volumes of water vapor, which in a confined space does not produce a great *decrease* in pressure. If the heat evolved is taken into account, however, the complete equation is as follows:



If we remember Gay-Lussac's law of gas pressure, and recall the fact that the specific heats of gases are very small, we shall see that the heat of reaction may lead to a greatly increased gas pressure, especially when the reaction is very rapid.

Explosive mixtures. A second fact not indicated by the equation of a reaction is that explosion of a gas mixture will not occur unless the mixture falls between certain limits in percentage composition. Thus, if hydrogen and air are mixed, the resulting mixture is not explosive unless the volume percentage of hydrogen is above 9 per cent and below 65 per cent. In mixtures outside of these limits the combination is so gradual, the heat is so largely absorbed by the excess gases present, and the pressure change takes place so slowly and is so small a fraction of the total pressure, that no explosion occurs. The following table gives both the lower and the upper limits of explosive mixtures of several gases with air, expressed in volume percentages. The values are to be regarded as roughly approximate.

Explosive Mixtures with Air

GAS	VOLUME PERCENTAGE AT LOWER LIMIT	VOLUME PERCENTAGE AT HIGHER LIMIT
Hydrogen, H_2	9	65
Methane, CH_4	5	13
Carbon monoxide, CO	14	74
Acetylene, C_2H_2	3	73
Water gas, $\text{H}_2 + \text{CO}$ (essentially) . .	12	66
Coal gas, $\text{H}_2 + \text{CH}_4$ (essentially) . . .	6	29

Mine explosions; the safety lamp. Some of the disastrous mine explosions that we read about are due to very finely divided particles of coal suspended in the air of the mine. These particles, if ignited, burn with explosive violence. Other mine explosions are due to the accumulation of methane in the air of the mine until an explosive mixture (*fire damp*) is formed. Fortunately the ignition point of a mixture of methane and air is high, and its flame may be extinguished by cooling. In 1815 Sir Humphry Davy (Fig. 190) invented a miner's lamp, based on this principle, in which the usual chimney of a lantern is replaced by a wire gauze (Fig. 290). An explosion flame starting at the wick is so cooled by the metal wire that ignition ceases, and the explosion is confined to the interior of the lamp. The principle may be demonstrated by holding a wire gauze a few inches above a Bunsen burner parallel with the table top

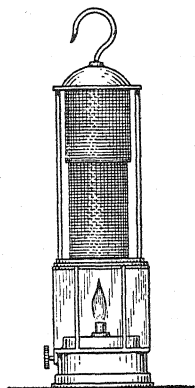


FIG. 290. *Miner's Safety Lamp*

(Fig. 291). When the gas is turned on and lighted *above* the gauze, the resulting flame rests upon the gauze but does not pass through it to the burner. The type of lamp just described has been replaced largely by small electric lights operated by pocket batteries.

Useful explosions. We commonly think of explosions as very destructive, as destroying buildings and killing people. When properly harnessed, however, they may be made our servants. Thus in the so-called internal-combustion engines used in all automobiles, the propelling agent is a mixture of gasoline vapor and air which is admitted to the cylinder and exploded by an electric spark (Fig. 292). The mixture of vapor and air is produced and controlled by the carburetor. The modern carburetor is complicated, but the principle involved is simple and is shown in Fig. 293.

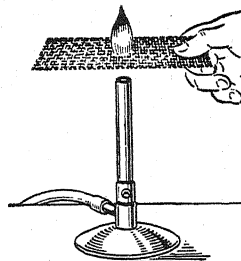


FIG. 291. *Illustration of the Principle of the Miner's Lamp*

Antiknock gasolines. The vapor from most gasolines, when mixed with air and exploded, as described in Fig. 292, produces a violent "knock" in the engine. This very objectional knock can be prevented by adding to the gasoline a small percentage (1 to 3 cc/gal of gasoline) of lead tetraethyl, $\text{Pb}(\text{C}_2\text{H}_5)_4$. Along with this is also added a small percentage of ethylene dichloride and ethylene dibromide (p. 314) in order to volatilize the lead so

that it will be carried out through the exhaust. Otherwise the lead would coat the spark plugs and other parts of the engine.

Ordinary gasolines, composed largely of hydrocarbon molecules with their carbon atoms arranged in a straight chain (thus : $\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-$),

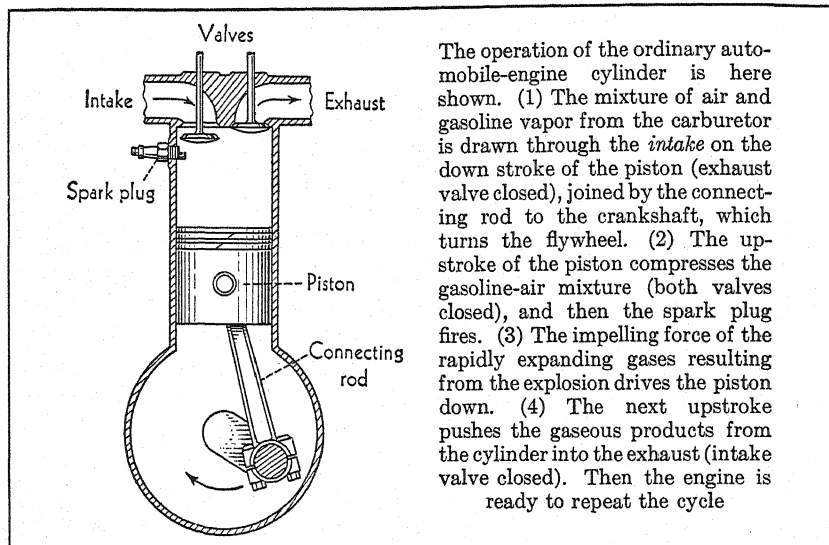
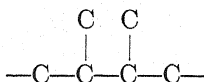


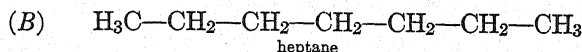
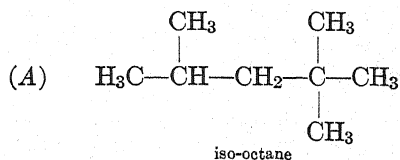
FIG. 292. Gasoline-Engine Cylinder

are prone to knock violently (unless lead tetraethyl is added) ; but the more highly branched chain molecules, such as



do not knock.

Antiknock rating. In the standard method for rating the antiknock value of a gasoline, the branched iso-octane (*A*) is arbitrarily assigned the value 100 per cent, while the straight chain heptane (*B*) is called 0 per cent :



The former is very much better and the latter somewhat worse in antiknock properties than ordinary gasoline. By making the proper blend of these

two and using it in an engine the intensity of knocking can be made to duplicate that of any gasoline to be tested. The percentage of iso-octane in the blend required to equal the behavior of gasoline under test is called the *octane number* of the gasoline.

The Diesel engine. None of our engines utilizes more than a small percentage of the energy in the fuel consumed. In the case

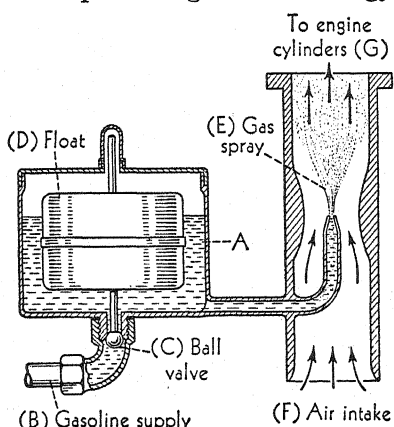


FIG. 293. *Diagram Illustrating the Principle of an Automobile Carburetor*

The gasoline enters the carburetor at B and is kept at a constant level in A by the float D and ball valve C. The gasoline issues as a fine spray from the jet E and forms an explosive mixture with the air drawn in at F. This mixture passes through G to the cylinders of the engine, where it is exploded by a spark

of the ordinary steam engine the efficiency is less than 10 per cent. If we could find a way of utilizing all the energy in gasoline, 1 gal of it would run our average automobile, traveling 30 miles an hour, 200 miles instead of the 15 to 20 actually covered. The modern Diesel engine, which is rapidly being developed and coming into wide use, is the most efficient type of engine; but even this does not utilize more than 40 per cent of the energy of the fuel consumed.

In this type of engine, air is admitted to the cylinder of the engine and is highly compressed by the stroke of the piston. As a result of this compression, so much heat is generated that the temperature reaches that of a red-hot stove. At the instant of greatest compression a fine spray of oil is forced

into the cylinder. The temperature of the hot air is sufficient to ignite the mixture of oil and air, and the resulting explosion forces the piston down and so runs the engine.

Blowpipes. A blowpipe is simply a device for burning a gas in pure oxygen. It consists essentially of two tubes, A and B, one inside the other, as shown in Fig. 294. The inflammable gas is forced through the outer tube and ignited at the tip C. Oxygen

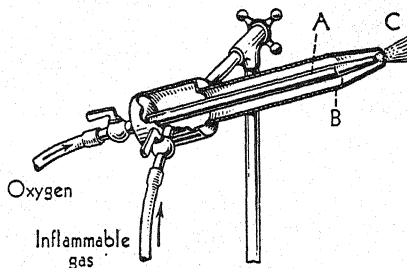


FIG. 294. *Diagram of Blowpipe*

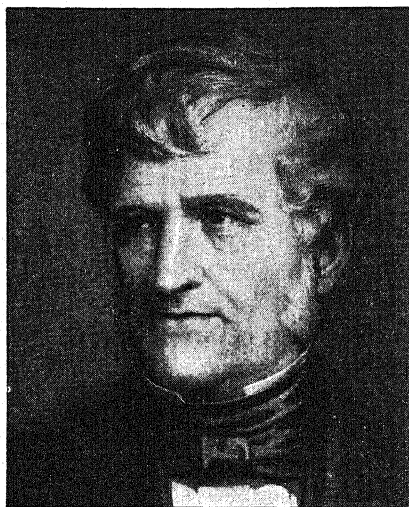


FIG. 295. *Robert Hare (1781-1858)*

An early American chemist who invented the oxyhydrogen blowpipe



FIG. 296. *Irving Langmuir (1881-)*

An eminent American chemist who has contributed much to our knowledge of atoms and molecules. In 1932 he was awarded the Nobel prize, generally regarded as the greatest honor that can come to any scientist

is then forced through the inner tube. The two gases are thus brought together at the tip of the tube and combine, with the evolution of so much heat that a temperature is reached sufficient to melt most metals.

The oxyhydrogen blowpipe. This is the oldest form of blowpipe and was devised by the American chemist Robert Hare (Fig. 295) in 1801. As the name suggests, the two gases used are oxygen and hydrogen. By proper adjustment a temperature of over 2000° may be reached. This form of blowpipe has largely given way to more efficient ones, although it is still used for certain purposes, as in the fashioning of vessels from quartz.

The oxyacetylene blowpipe. This is a device for burning acetylene in an atmosphere of oxygen. It gives a very hot flame (above 3000°) because to the heat of combustion of the carbon and hydrogen is added the heat of decomposition of the acetylene (see acetylene). This form of blowpipe is especially adapted to the welding and cutting of metals, although it has the disadvantage that a metal in contact with the flame may combine with the carbon present in the flame. In dismantling iron structures, the tip of the flame is held in contact with some part of the metal until the latter is heated to a high temperature. Additional oxygen is then turned on, and the hot metal at once begins to burn. By slowly moving the tip of the flame containing the excess of oxygen over the metal, the latter is cut into pieces.

The atomic hydrogen blowpipe. An interesting modification of the oxyhydrogen blowpipe, devised by Langmuir (Fig. 296), develops a very high temperature suited to welding and cutting metals. A stream of hydrogen gas issues from a small copper tube through an electric arc maintained between tungsten electrodes, and is thereby dissociated into *atomic* hydrogen. As this atomic hydrogen emerges from the arc, it burns as a fine flame to form molecular hydrogen. This flame is in turn surrounded by an external cone of molecular hydrogen burning in oxygen. The resulting flame has a temperature of at least 6000° . This flame has the additional

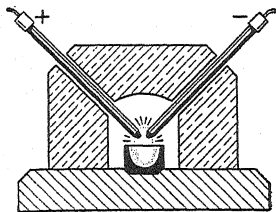


FIG. 297. *An Electric Arc Furnace*

advantage that it is reducing in character and so prevents the oxidation of the metals being melted or welded.

The blast lamp. This form of blowpipe, used in all laboratories, is a device for burning some form of fuel gas in air. Since air is used in place of pure oxygen, the flame is not so hot as in other forms of blowpipes; but the temperature reached is sufficient for most laboratory purposes, and its convenience makes it a part of all laboratory equipment.

The electric furnace. Electric furnaces have come into wide use in operations requiring a very high temperature. Temperatures as high as 3500° can easily be reached, whereas the hottest oxyhydrogen flame is not much above 2000° . These furnaces are constructed on one of three general principles.

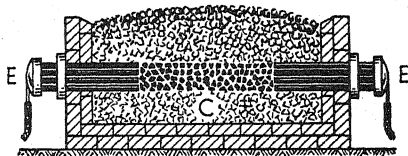


FIG. 298. *An Electric Resistance Furnace*

1. **Arc furnaces.** In one type the source of heat is an electric arc formed

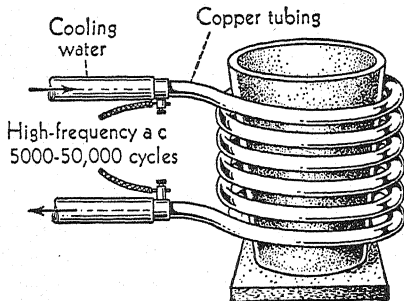


FIG. 299. *An Electric Induction Furnace*

between carbon electrodes separated a little from each other, as shown in Fig. 297. The substance to be heated is placed in a vessel, usually a graphite crucible, just below the arc. The electrodes and crucible are surrounded by materials which resist fusion, such as magnesium oxide, and the walls of the furnace are so shaped as to reflect the heat downward upon the contents of the crucible.

2. **Resistance furnaces.** In a second type of furnace the heat is generated by the resistance offered to the

current in its passage through the furnace. In its simplest form it may be represented by Fig. 298. The furnace is merely a rectangular box built up

of loose bricks. The electrodes E, E , each consisting of a bundle of carbon rods, are introduced through the ends of the furnace. The materials to be heated (C) are filled into the furnace up to the electrodes, and a layer of broken coke is arranged so as to extend from one electrode to the other. More of the charge is then placed on top of the coke. In passing through the broken coke the electric current encounters great resistance. This changes much of the electrical energy into heat, and the charge surrounding the coke is brought to a very high temperature. The advantage of this type of furnace is that the temperature can be regulated to any desired intensity.

3. **Induction furnaces.** The so-called *induction* furnaces are now largely used for heating *conducting* materials. In these the metal to be melted is placed in a ceramic crucible around which is coiled a copper tube through which a current of cold water flows (Fig. 299). A high-frequency electric current is passed through the metal of the tube and *induces* electric currents inside the body of material to be melted. Such induced currents rapidly raise the temperature of the body in which they are set up.

Questions

1. (a) How would you define a flame? (b) Why does water gas burn with a nonluminous flame?
2. (a) What is the difference between the temperature of a flame and the heat of the flame? (b) Does a knowledge of the one inform you about the other?
3. (a) What is the probable source of the nitrogen in natural gas? (b) Would a cubic foot of natural gas containing 5 per cent of nitrogen give as much heat when burned as a cubic foot free from nitrogen?
4. What is the difference between calorific value and heat of combustion?
5. Why should anthracite and coke be considered more desirable for domestic furnaces than soft coal?
6. Is an oxidizing flame different from a reducing flame, or is it the region of the flame in which the difference lies?
7. In stating the heat of combustion of hydrogen burning in oxygen, why is it necessary to specify whether the resulting water was a vapor or a liquid?
8. Would a miner's safety lamp with a chimney of woven glass or asbestos fibers be a success?
9. Why do the windows of a gas-heated room so often "sweat" in cold weather?

Problems

1. (a) What weight of Connellsville anthracite will have the same caloric value as a ton of Pocahontas coal? (b) Aside from transportation costs, would the market price of these two varieties of coal be in the same ratio?

2. How much methane would have to be burned to have heating value equal (a) to 1000 g of acetylene; (b) to 1000 g of hydrogen?

3. In a room 15 ft \times 12 ft \times 10 ft there is a stove that burns 9 cu ft of natural gas per hour. The stopcock was accidentally turned on with the stove unlighted. Assuming that the gas was pure methane, calculate the approximate time that the gas must escape before an explosive mixture will be formed. (Assume that the amount of air in the room remains constant.)

4. A gas stove burning 6 cu ft of methane per hour is not connected with a chimney. (a) What weight of carbon dioxide will escape into the room if the stove burns for 7 hours? (b) What volume will this occupy at 20° and 750 mm pressure? (c) What weight of water vapor will be formed?

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Consult the Minerals Yearbook for an annual review of the natural gas industry

Carbohydrates; Alcohols; Coal-Tar Compounds

Carbohydrates. In Chapter 9 it was pointed out that the products of *photosynthesis*, in the green leaf, are oxygen and carbohydrates. The term *carbohydrate* is applied to a class of compounds which includes the sugars, starch, and allied substances. These compounds contain carbon, hydrogen, and oxygen, and in most of the common members of the group the hydrogen and oxygen are present in the proportion in which they combine to form water. The carbohydrates are not only the probable original sources of all our body and fuel energy, but also the starting materials out of which plants and animals make synthetically practically all the many organic compounds found in nature. The most important carbohydrates are the following:

Table of Important Carbohydrates

Sucrose (ordinary sugar)	$C_{12}H_{22}O_{11}$
Lactose (milk sugar)	$C_{12}H_{22}O_{11} \cdot H_2O$
Maltose (malt sugar)	$C_{12}H_{22}O_{11} \cdot H_2O$
Glucose (grape sugar)	$C_6H_{12}O_6$
Fructose (fruit sugar)	$C_6H_{12}O_6$
Starch	$(C_6H_{10}O_5)_x$
Cellulose	$(C_6H_{10}O_5)_x$

The molecular formulas of cellulose and starch are unknown but are multiples of the simple formula $C_6H_{10}O_5$; accordingly they are often written $(C_6H_{10}O_5)_x$, in which x is somewhere between 26 and 30 for starch and 100 and 200 for cellulose.

Isomeric compounds. It will be noted that some of the compounds named in the table have identical formulas. *Compounds that have the same molecular formulas are said to be isomeric.* Thus, glucose and fructose are isomeric compounds. The difference in the properties of isomeric compounds is due to the fact that the atoms are arranged differently in the molecules (Fig. 300). Just as two houses may be entirely different and yet be built from the same kind and the same number of bricks, so two compounds may be different and yet the molecules of each may contain the same elements and the same number of atoms of each element.

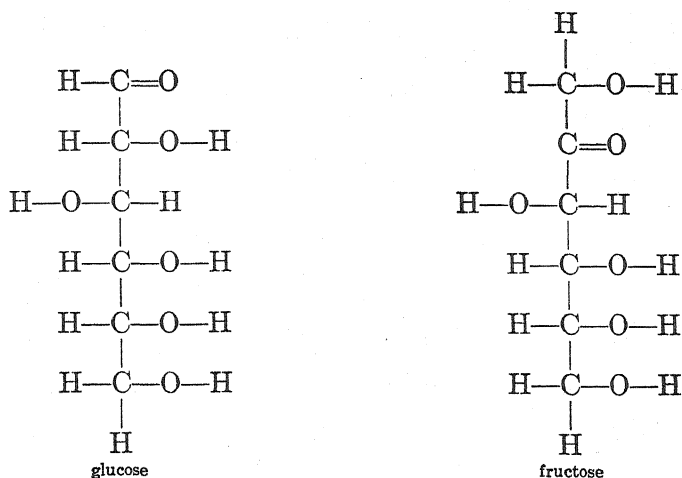
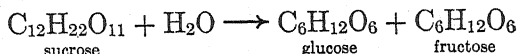


FIG. 300. *Formulas of Two Isomeric Compounds*

Sucrose (sugar) ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$). A great many different sugars are known. *Sucrose*, or ordinary *sugar*, is the most familiar of these. This compound, known from very ancient times, occurs in many plants, especially in the sugar cane and sugar beet; and these two plants practically furnish the world's supply. The sugar cane grows only in warm climates (Cuba and the Hawaiian Islands are the greatest producers), while the sugar beet thrives in cooler climates, such as prevail in Colorado and Nebraska in the United States, and in Germany. The terms *cane* and *beet*, when applied to sugar, simply indicate the *source* of the product. From either source it is the same compound, namely, sucrose.

The separation and refining of sugar. Sugar cane contains from 12 to 15 per cent of sucrose, and the sugar beet from 15 to 20 per cent. The juice extracted from these plants contains the sugar in solution along with many impurities. These impurities are removed, and the solution is then evaporated until the sugar crystallizes. The evaporation is conducted in closed vessels from which the air is partly exhausted (vacuum pans). In this way the boiling point of the solution is lowered, and the charring of the sugar is prevented. It is not practicable to remove all the sugar from the solution. Ordinary *molasses* is the solution which remains after a part of the sugar has been crystallized from the purified juice of the sugar cane. *Brown sugar* is partially purified cane sugar. Beet sugar requires more elaborate purification than cane sugar. The sweetness of *maple sugar* is due to sucrose; the distinctive flavor is imparted by other substances present in the maple sap. The annual consumption of sucrose in the United States amounts to a little more than 100 lb for each inhabitant.

Chemical conduct of sucrose. When a solution of sucrose is heated to about 70° with water and hydrochloric acid (which acts as a catalyst), the two isomeric sugars, *glucose* and *fructose*, are formed in accordance with the following equation :



In this process the sugar is said to be *inverted*, and the mixture of glucose and fructose is termed *invert sugar*.

When heated to 186° , sucrose melts; if the temperature is increased to about 215° , a partial decomposition takes place, and a brown substance known as *caramel* is formed. This is used extensively as a coloring matter and in making confectionery.

Lactose (milk sugar) ($\text{C}_{12}\text{H}_{22}\text{O}_{11} \cdot \text{H}_2\text{O}$). *Lactose* occurs in the milk of all mammals. The average composition of cow's milk is as follows :

Water	87.0%
Casein (nitrogenous matter)	3.3%
Butter fat	4.0%
Lactose	5.0%
Mineral matter	0.7%

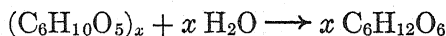
When *rennin* (a substance obtained from a calf's stomach) is added to milk, the casein and fat precipitate. These are separated and used in the manufacture of *cheese*. Large amounts of casein are also used in the printing of wallpaper and fabrics, and for making artificial wool, glue, and plastic material similar to hard rubber. The liquid remaining after the separation of the casein and fat is known as *whey*. This contains the *milk sugar*, which is easily obtained in a pure state; it resembles sucrose in appearance, but is not so soluble and is only about one fourth as sweet. The souring of milk is the result of the conversion of the milk sugar into *lactic acid*, a liquid compound whose formula is $\text{H} \cdot \text{C}_3\text{H}_5\text{O}_3$. This change is known as *lactic fermentation* and is caused by certain bacteria. These bacteria (or their spores) are everywhere present in the air and are associated especially with dust and dirt; hence extreme cleanliness will greatly delay the souring of milk. Sweet milk heated to about 65° for forty minutes is said to be *pasteurized*. The heat destroys any disease-producing bacteria present; and if the air is excluded from it, *pasteurized milk* will keep sweet for some days.

Maltose ($\text{C}_{12}\text{H}_{22}\text{O}_{11} \cdot \text{H}_2\text{O}$). This sugar resembles sucrose in its general properties but is only about half as sweet. It is prepared by the action of malt upon starch—hence the name *maltose*.

Malt is the name applied to barley which has been moistened, kept in a warm place until it has germinated, and then heated until the vitality of the grain has been destroyed. In the process of germination a substance is formed known as *diastase*, and it is this substance which gives malt its property of changing starch into maltose. The *ptyalin* in saliva brings about a similar change in the starch present in our foods.

Enzymes. Many processes of fermentation and hydrolysis taking place in organic materials are due to a peculiar class of catalysts called *enzymes*. These are products of living cells, and are very complex organic compounds. Diastase and ptyalin (mentioned in the preceding paragraph) are examples of enzymes. Enzymes are remarkable specialists, and each variety brings about its own particular change in some one type of compound.

Glucose (grape sugar, dextrose) ($C_6H_{12}O_6$). *Glucose* is present in many fruits. It is usually associated with fructose and is often called *grape sugar* because of its presence in grape juice. Commercially it is prepared by heating starch with water to which hydrochloric acid (a catalyst) has been added:



When the change is complete, enough sodium carbonate is added to neutralize the hydrochloric acid, and the solution is then evaporated.

Pure glucose is a white crystalline solid which resembles sucrose in its properties but is only about half as sweet. It constitutes an inexpensive and healthful food. A small percentage is present in the blood of persons in good health, and a much larger percentage in the blood of persons afflicted with diabetes.

Corn sirup (commercial glucose). In preparing glucose from starch, if the process is stopped before complete conversion takes place, there is obtained a thick sirup known commercially as *corn sirup*, or *glucose*. This is really an aqueous solution of glucose and maltose, and a mixture of other carbohydrates called *dextrin*, formed by heating starch. It is prepared in enormous quantities for use as a constituent of candies, jellies, jams, sirups, and other sweets.

Fructose (fruit sugar, levulose) ($C_6H_{12}O_6$). *Fructose* is a white solid which occurs, along with glucose, in fruits and honey. It is even sweeter than sucrose, and has the general properties of a sugar.

Starch, ($C_6H_{10}O_5$)_x. This compound is one of the most abundant carbohydrates found in nature and is especially abundant in seeds and tubers. In the United States it is obtained chiefly from corn, about 60 per cent of which is starch. In Europe it is obtained prin-

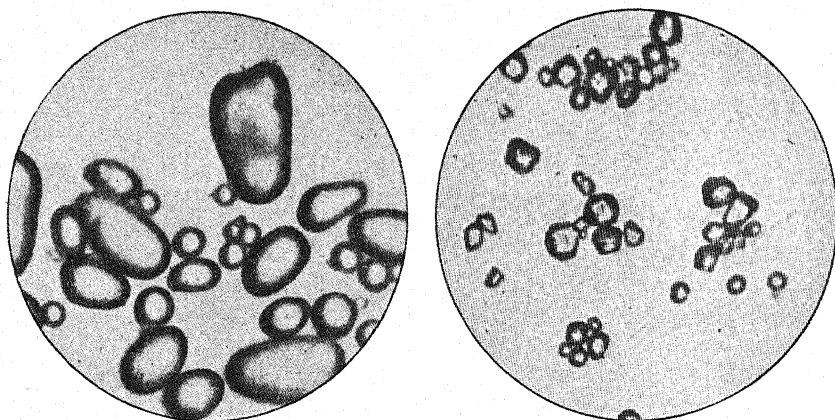


FIG. 301. View of Granules of Wheat Starch (at Left) and of Corn Starch (at Right)
Magnified 290 times

cipally from the potato. Starch consists of minute granules which vary in size and characteristics according to their source, so that anyone familiar with them can tell the source of any given sample of starch by examining it through the microscope (Fig. 301).

Starch does not dissolve in cold water to any extent. If heated in water the starch granules burst open, forming *starch paste*. Cold hydrochloric acid slowly converts it into *soluble starch*. Iodine imparts a blue color to starch (p. 318), and this color change serves as a simple test for the presence of starch in foods.

Cellulose ($C_6H_{10}O_5$)_x. *Cellulose* constitutes the main part of the cell walls of plants. Cotton is about 90 per cent cellulose, and ordinary woods from 40 to 65 per cent. The properties of cellulose can be judged by those of ordinary filter paper, which is nearly pure cellulose. It is insoluble in all ordinary solvents, but is readily converted into soluble derivatives. A cold concentrated solution of sodium hydroxide gives a silklike appearance to cellulose, and advantage is taken of this fact in the manufacture of *mercerized cotton*. Concentrated hydrochloric acid converts cellulose into glucose:



Cellulose nitrates (nitrocellulose); cellulose acetate. Cellulose contains a number of hydroxyl radicals. When the compound is treated with nitric acid containing some sulfuric acid, the acid reacts with the cellulose much as it does with a base, forming water and a mixture of covalent compounds called *cellulose nitrates* but often

known collectively as *nitrocellulose*. The sulfuric acid used along with the nitric acid assists the reaction by combining with the water formed. If the action is not pushed too far, the product contains from 10 to 12.5 per cent of nitrogen and is soluble in a mixture of ordinary alcohol and ether; if the action is continued, the nitrogen content of the product is increased, amounting to from 12.5 to 13.5 per cent. This product is insoluble in an alcohol-ether mixture and is often referred to as *guncotton*. The cellulose nitrates are all inflammable white solids and under certain conditions are highly explosive.

When cellulose is treated with acetic anhydride, *cellulose acetate* is formed. This has many of the properties of cellulose nitrate and is adapted to the same general uses. While it is more expensive than the nitrate, it has an added advantage for many purposes in that it is not so inflammable and is not explosive.

The uses of cellulose nitrate. Cellulose nitrate has many uses, the most important of which are the following: (1) It is the chief constituent of *smokeless gunpowders*. (2) *Photographic films* are made from it, as well as from cellulose acetate. (3) It is the basic material in the *lacquers* that have come into such wide use in recent times, especially in the automobile industry. (4) Leatherlike products, used for bookbinding, automobile cushions, and handbags, consist of a canvas base (or other strong material) impregnated and coated with cellulose nitrate. (5) *Collodion* is a solution of cellulose nitrate in a mixture of alcohol and ether and is used as a covering for wounds in place of court plaster. (6) *Celluloid* and similar preparations are mixtures of cellulose nitrate and camphor (or some similar material). The latter is a white solid obtained from the camphor tree, which grows in Oriental countries. (More than half of the 500,000 lb of camphor used annually in this country for various purposes is now made synthetically from the pinene oil obtained from turpentine.) When the nitrate and camphor are mixed together, a plastic mass is formed which can be molded into any desired shape and when hard is used for making such objects as combs and brush handles. While the natural color of celluloid is white, it can be tinted any desired color with dyes and can also be obtained in transparent form. Because of the cellulose nitrate present, celluloid is inflammable, and many serious accidents have resulted from bringing it near a hot flame.

Rayon. Because of the high cost of natural silk (a product of the silkworm) efforts have long been made to produce from cellulose a cheaper product which would have the appearance and possess the properties of natural silk. The French chemist Count de Chardonnet seems to have been the first to solve the problem, and the first so-called artificial silk made by Chardonnet's process was exhibited at the Paris Exposition of 1889. For many years the industry made little progress, but in recent years it has grown enormously. For example, the present production in the United States is about 300,000,000 lb annually.

Commercial production of rayon. About three fourths of the rayon produced in the United States is made by the so-called *viscose* method. The

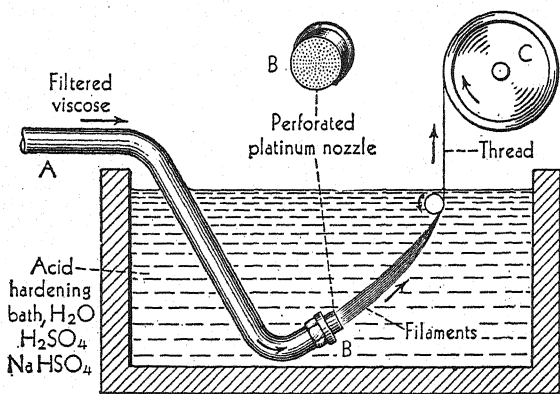


FIG. 302. Making Rayon Threads

(Fig. 302) and the perforated nozzle *B* (shown both sidewise and in cross section) into the hardening bath, which consists of a solution of sulfuric acid and sodium acid sulfate. The viscose emerges into the hardening bath in the form of fine streams, each of which is changed into a *filament* of regenerated cellulose immediately on coming in contact with the bath. These filaments are twisted into a thread of rayon by the devices shown in the figure. The number of perforations in the nozzle *B* determines the number of filaments, and these in turn the size of the thread.

Cellophane. Cellophane, which now has so many uses, has the same composition as rayon and is made by the same general method, except that the viscose is forced into the hardening bath in the form of a thin, wide stream, under conditions which cause it to produce sheets of transparent cellulose. If desired, these sheets may be made waterproof by a thin coating of a mixture of nitrocellulose lacquer and waxes. Both rayon and cellophane are composed of cellulose containing a small percentage of water.

Nylon. This newcomer in the field of textiles will be described in Chapter 29, after we have studied the compounds from which it is made.

Characteristics of various textile fibers. Of the natural fibers used in making the yarns from which the common fabrics are prepared, the vegetable fibers, cotton and linen, are essentially cellulose, while the animal fibers, wool and silk, are nitrogenous substances (proteins). Although these fibers resemble one another, more or less, when viewed with the naked eye, their appearance is distinctive when examined with the microscope (Fig. 303). It is also possible to distinguish between the fibers by the action of chemical reagents.

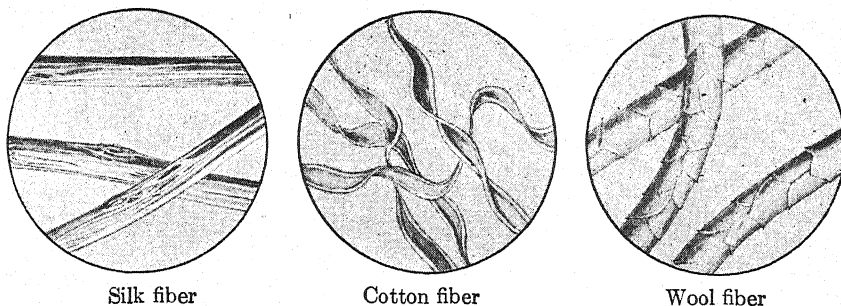


FIG. 303. *Some Textile Fibers*
Highly magnified

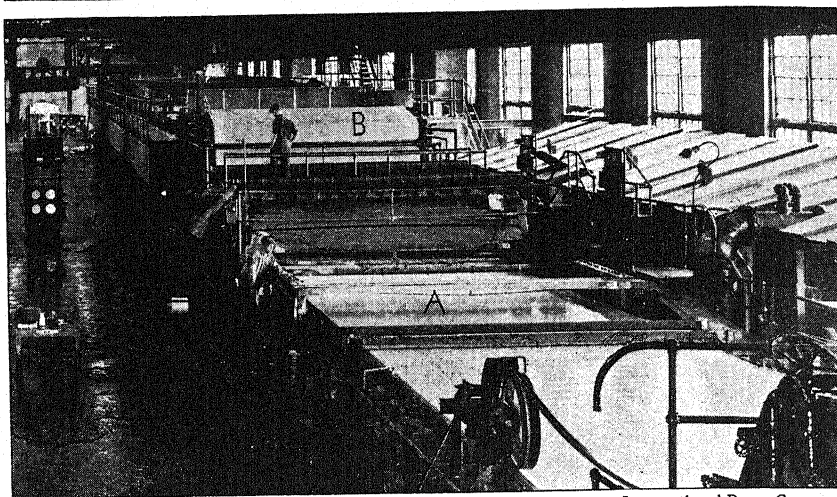
For example, a hot solution of sodium hydroxide containing from 5 per cent to 10 per cent of the hydroxide has but little action upon cotton, while it will readily dissolve wool and slowly dissolve silk.

Paper. Paper is composed essentially of "a large number of small, hair-like cellulose fibers, matted and interwoven so closely that they form a continuous surface." The most expensive papers are made from cotton rags, but by far the greatest quantity of paper is made from wood pulp, the fiber of wood.

Briefly the method most largely used in the manufacture of paper is as follows: The pulp is first prepared by cutting the wood (mostly spruce, pine, hemlock, and balsam) into small chips, which are then "cooked" with a solution of calcium hydrogen sulfite or sodium hydroxide in order to remove the noncellulose constituents. The product is next washed with water and bleached. The resulting pulp consists of wood fibers which are fairly pure cellulose. Certain substances, such as clay, alum, and resin, are then mixed with the pulp, the choice depending on the properties desired in the finished paper. The mixture of pulp, added substances, and water is next flowed onto a traveling belt of wire cloth in such a way as to form a sheet of paper (*A*, Fig. 304) from which the water is removed, first by pressure over endless woolen belts (*B*, Fig. 304) and then by carrying the sheet around hot metal cylinders shown in the background of the figure.

ALCOHOLS

Definition. The alcohols are compounds which may be regarded as derived from hydrocarbons by substituting for one or more hydrogen atoms of the hydrocarbons an equal number of hydroxyl groups. A great many alcohols are known, and, like the hydrocarbons, they may be arranged in series. The relation between the first four mem-



International Paper Company

FIG. 304. View of One Type of Paper Machine

bers of the methane series of hydrocarbons and the corresponding alcohols is shown in the following table :

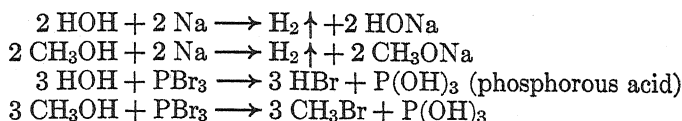
CH_4 (methane)	$\text{CH}_3\text{—OH}$ (methyl alcohol, methanol, wood alcohol)
$\text{CH}_3\text{—CH}_3$ (ethane)	$\text{CH}_3\text{—CH}_2\text{—OH}$ (ethyl alcohol, ethanol, ordinary alcohol)
$\text{CH}_3\text{—CH}_2\text{—CH}_3$ (propane)	..	$\text{CH}_3\text{—CH}_2\text{—CH}_2\text{—OH}$ (propyl alcohol)
$\text{CH}_3\text{—CH}_2\text{—CH}_2\text{—CH}_3$ (butane)		$\text{CH}_3\text{—CH}_2\text{—CH}_2\text{—CH}_2\text{—OH}$ (butyl alcohol)

The terms *methyl*, *ethyl*, *propyl*, and *butyl*, used in designating the different alcohols, are names applied to the univalent radicals CH_3 , C_2H_5 , C_3H_7 , and C_4H_9 respectively. It will be noted that the names of these radicals are derived from the names of the corresponding hydrocarbons by changing the ending -ane to -yl.

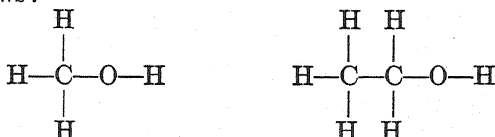
How structural formulas are deduced. The structural formula of a compound is often deduced from the chemical behavior of its molecule. Its molecular formula is first determined by the methods already described (p. 261). Knowing the molecular formula and the chemical reactions that the compound undergoes, we can generally get at least a clue as to how the atoms are arranged in the molecule; we can then test the accuracy of the formula so deduced by further chemical reactions.

As an example, suppose we wish to determine the structural formula of methyl alcohol. Its molecular formula is first established as described on page 79, and is found to be CH_4O . By experiments we find that sodium and also phosphorus tribromide react with methyl alcohol, just as with water. But the water molecule must contain a hydroxyl (OH) radical because in no other way can the 2 atoms of hydrogen and the oxygen atom

in the molecule be arranged than that shown in the formula $\text{H}-\text{O}-\text{H}$. Since both sodium and phosphorus tribromide react alike with water and methyl alcohol, we assume that the methyl alcohol molecule, like that of water, contains a hydroxyl radical; and we write its formula tentatively CH_3OH . That this formula will account for the similarity of the reactions of water and methyl alcohol is shown in the following equations:



Since all the other reactions of methyl alcohol can best be explained upon the assumption that its formula is CH_3OH , we accept it as true. Then, since the valences of carbon, hydrogen, and oxygen are respectively 4, 1, and 2, the atoms in CH_4O (and similarly in ethyl alcohol, $\text{C}_2\text{H}_6\text{O}$) must be arranged as follows:



Structural formulas are presented for the sake of giving the student an impression of the architecture of the molecules of a few important compounds. Just as the drawn plans of a house give us more information about the house than simply a statement of the materials that enter into its construction, so the structural formula of a compound tells us more about it than its molecular formula. Of course the more complex a compound, the more difficult it is to determine its structural formula; but the principle involved is the same as that given above for methyl alcohol.

Methyl alcohol (methanol, wood alcohol) (CH_3OH). This compound is a typical alcohol, and is often called *methanol* to avoid confusion with ordinary alcohol. Methyl alcohol is formed when hard woods, especially beech and birch, are heated in the absence of air (p. 454); hence the name *wood alcohol*. Wood distillation long furnished us with our entire supply of methyl alcohol, 1 ton of wood yielding a little less than 2 gal. In 1927, however, a synthetic method of preparation was perfected, and at present is the principal source of this compound. The synthetic product is prepared by heating a mixture of carbon monoxide and hydrogen under pressure and in contact with a suitable catalyst, such as the oxides of zinc and chromium:



Methyl alcohol is a colorless liquid which boils at 64.5° . It is lighter than water and mixes with it in all proportions. It burns with an almost colorless flame. It is a good solvent for organic substances and is used in the manufacture of varnishes. Its chief use is in the manufacture of formaldehyde (p. 511) and aniline dyes, and as a denaturant (p. 510) for ordinary alcohol. It is poisonous, and many deaths have resulted from its use as an intoxicant. It has a specific action on the optic nerve, and many cases of blindness have resulted from drinking the liquid or from inhaling its vapor.

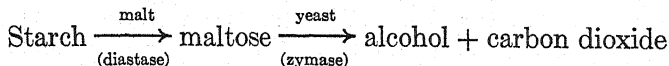
Ethyl alcohol (ethanol, ordinary alcohol) (C_2H_5OH). This is the colorless liquid commonly designated as *alcohol*.

1. **Preparation.** Ethyl alcohol is prepared by the action of ordinary brewer's yeast upon certain sugars, especially maltose and dextrose. With dextrose the reaction is expressed thus:



This process, in which a sugar is changed into alcohol and carbon dioxide by the action of yeast, is known as *alcoholic fermentation*. The yeast is a simple form of plant life which grows in the sugar under suitable conditions. During its growth it secretes an enzyme known as *zymase*, which is the active agent in the breaking down of the sugar into alcohol and carbon dioxide. The yeast acts, therefore, as a sort of factory for producing zymase. While sucrose does not ferment directly, the addition of yeast to its aqueous solution first resolves the sucrose into glucose and fructose, both of which then ferment.

Alcohol may also be prepared from starch by adding, first, malt, which changes the starch into maltose, and then yeast, which sets up alcoholic fermentation, forming alcohol and carbon dioxide:



Commercial method for preparing ethyl alcohol. Nearly all the alcohol made for commercial use in the United States is prepared by the fermentation of the sugar in crude molasses. The molasses is shipped from Cuba in large quantities for this purpose.

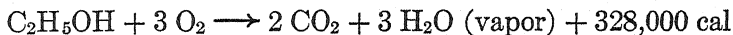
If sufficient sugar is present, it is possible to obtain by direct fermentation an aqueous solution containing from 15 to 20 per cent of alcohol. By fractional distillation this may be concentrated to a solution containing 96 per cent of alcohol. When lime (CaO) is added to this solution, and the mixture heated, most of the remaining water combines with the lime to form calcium hydroxide. Upon distilling the resulting mixture, alcohol

containing less than 1 per cent of water distills over. This product is termed *absolute alcohol*. The ordinary alcohol of the druggist contains approximately 93 per cent by weight of alcohol and 7 per cent of water.

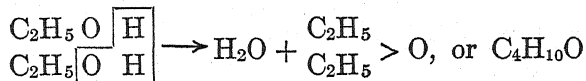
Absolute alcohol is prepared on a large scale by adding benzene to the 90 to 95 per cent alcohol and distilling the mixture. At first the benzene, water, and some alcohol distill over, followed by the absolute alcohol. While the process is simple in practice, the explanation is beyond the scope of an introductory text.

Just as methyl alcohol can be prepared from carbon monoxide and hydrogen, so ethyl alcohol can be prepared from certain gases obtained in the cracking of petroleum (p. 471). It is possible that the ethyl alcohol of the future may be prepared in this way; indeed, some of it is so prepared at the present time.

2. Properties. Ethyl alcohol is a colorless liquid and has a characteristic odor different from that of methyl alcohol. It has a density of 0.789 at 20°, boils at 78.5°, and solidifies at - 117.3°. It resembles methyl alcohol in its general properties. When ignited it burns with a hot flame:



It is sometimes used as a source of heat, since it does not deposit carbon, as does the flame from oils. When taken into the system in small quantities it causes intoxication; in larger quantities it acts as a poison. The intoxicating properties of such liquors as beer, wine, and whisky are due to the alcohol present. When heated to 140° with sulfuric acid, alcohol loses the elements of water, forming *ethyl ether* (ordinary *ether*), as shown in the following equation:



Ether is a colorless liquid boiling at 34.5° and is largely used as an anesthetic in surgical operations.

Alcoholic liquors. All alcoholic liquors are made by alcoholic fermentation. Wine is made by the fermentation of the glucose in grape juice and contains from 5 to 15 per cent by volume of alcohol. Beer is made from maltose, formed by the action of malt upon starch obtained from various grains, chiefly barley. It contains from 3 to 6 per cent by volume of alcohol. Whisky contains about 50 per cent by volume of alcohol and is made from starch by a process very similar to that described in connection with the commercial preparation of alcohol. When first prepared whisky contains a small percentage of higher-boiling alcohols which are very poisonous. On

long standing (*aging*) these react with other constituents present to form compounds which give to whisky its characteristic flavor. Almost any saccharine liquid, such as cider or fruit juices in general, when exposed to air, gradually undergoes alcoholic fermentation; for spores of the yeast plant enter from the air.

The physiological effects of methyl alcohol and of ethyl alcohol. There has been so much discussion in regard to the poisonous properties of these two alcohols that the following statement of the results of careful experiments may not be out of place: If taken in a single large dose, ethyl alcohol is slightly more poisonous than methyl alcohol. If taken in smaller amounts over a period of days, however, methyl alcohol is much the more poisonous. The reason for this is that the ethyl alcohol is oxidized in the system to water and carbon dioxide, which produce no serious effects, while the methyl alcohol oxidizes to formic acid, which accumulates in the system and, if the doses are continued, ultimately produces death.

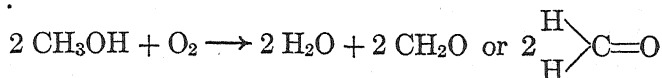
Denatured alcohol. Practically all governments lay a very heavy tax on alcoholic beverages, and upon alcohol as well, since beverages in imitation of fermentation beverages can be made from alcohol very easily. Alcohol has many important *industrial* uses, however, and no government wants to impede legitimate industrial progress. To make alcohol available for industry, while preventing its use in beverages, the Federal government allows *denatured* alcohol to be sold tax-free.

Denatured alcohol contains certain added substances in solution which render it unfit for beverage purposes but do not impair its value for industrial uses. The substances which may be used for this purpose are called *denaturants* and are definitely prescribed by law. The most usual denaturants are *methyl alcohol* (which must be obtained by wood distillation), *benzine*, and a product of the oxidation of kerosene called *aldehyol*. Pure alcohol can also be purchased tax-free by educational institutions for scientific purposes.

Production and uses of ethyl alcohol. More than one hundred million gallons of alcohol (calculated as 100 per cent C_2H_5OH) is produced annually in the United States, most of which is denatured for various uses. Nearly one third of the total product is used as an antifreeze in automobile radiators in winter. Large quantities are also used in the manufacture of the various products made from cellulose and in the manufacture of vinegar, lacquers, shellacs and varnishes, toilet preparations, drugs, and various chemicals and dyes.

Aldehydes. When treated with suitable oxidizing agents, alcohols are converted, by loss of hydrogen, into compounds known as *aldehydes*. One of the most important members of this group is

formaldehyde (CH_2O), which is prepared by the oxidation of methyl alcohol :



Formaldehyde is a gas, and an aqueous solution containing not less than 37 per cent by weight of the gas is sold by druggists under the name of *formalin*. It is of great importance in the manufacture of resins (such as *Bakelite*) and dyes. It is also a common and efficient disinfectant.

Chemical changes in breadmaking. The average composition of wheat flour is as follows :

Water	11.9 per cent
Protein (nitrogenous matter)	13.3 per cent
Fats	1.5 per cent
Starch	72.7 per cent
Mineral matter	0.6 per cent

In making bread, flour is mixed with water, yeast, salt, and a little sugar, and the resulting dough is set aside in a warm place for a few hours. The yeast first causes the sugar to undergo alcoholic fermentation. The carbon dioxide formed escapes through the dough, making it light and porous. The yeast plant thrives best at about 30° ; hence the necessity for keeping the dough in a warm place. In baking bread the heat expels the alcohol and also expands the bubbles of carbon dioxide caught in the dough, causing it to become more porous and making the bread light.

Preservatives. We have observed that the changes taking place in the souring of milk and the changing of sugar into alcohol are caused by microorganisms, the spores of which are present in the air. Many other similar changes, such as putrefaction, are due to the same cause. All these changes may be prevented in one of the following ways :

1. The substance may be kept at such a low temperature that the organism causing the change cannot thrive (cold storage). "Quick-frozen" foods, which retain most of their flavor and natural color indefinitely, are an interesting recent development. The foods are generally packaged and frozen quickly from 5° to -30°F ; and marketed in the frozen state. In 1938 it is estimated that about 250,000,000 lb of vegetables, fruit, and meat of all kinds were prepared and marketed in this way in the United States; and the industry is growing very rapidly.

2. The substance may be heated so as to destroy all organisms present, and may then be sealed airtight in a suitable container. This is the method used in canning vegetables and in preserving such substances as condensed milk.

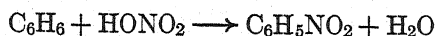
3. Some substance may be added which in small quantities will destroy the organisms causing the change or will prevent their growth. Such a substance is known as a *preservative*.

Whether or not preservatives should be permitted in foods is a much-debated question. Some people maintain that any substance which is powerful enough to prevent the growth of the organisms must have an injurious action upon digestion. The Federal government at present allows the use of *sodium benzoate* (a white solid made from a hydrocarbon present in coal tar) in such foods as jellies, jams, and catchup, which are not consumed immediately upon the opening of the container. If this preservative is used, however, the labels on the containers must state the amount present.

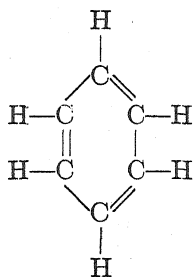
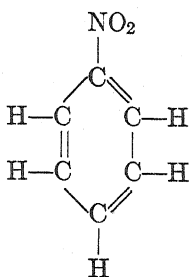
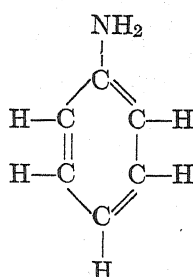
THE COAL-TAR COMPOUNDS

Coal tar and the coal-tar compounds. In connection with the manufacture of coal gas (p. 482) we learned that along with the gas, coke, and ammonia there is formed a thick, tarry liquid known as *coal tar*. This liquid is composed of a mixture of a large number of compounds and serves as the commercial source of some eight or ten important ones. These are obtained from the coal tar by fractional distillation in a manner entirely analogous to fractioning petroleum. Each of the compounds so obtained serves as the source material from which many other useful compounds are prepared. *There are many thousands of these compounds; and all of them, whether obtained directly from coal tar or prepared from others so obtained, are known collectively as the coal-tar compounds.* It is possible here to mention only a very few of the most important of these, as follows:

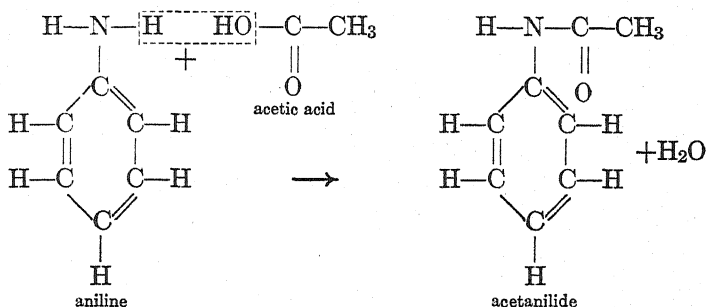
1. **Benzene (C_6H_6).** This hydrocarbon is a colorless liquid boiling at 79.6° , and is a good solvent for most organic compounds, so that it is very useful in the laboratory. Both the liquid and its vapor are highly inflammable. One gram-molecule of the liquid on combustion evolves 783,400 cal if the water formed is kept in a state of vapor. Benzene is used to a limited extent in place of gasoline in gasoline engines. It reacts readily with nitric acid, forming *nitrobenzene* ($C_6H_5NO_2$), a slightly yellowish liquid often called oil of mirbane:



When nitrobenzene is reduced with hydrogen, *aniline* ($C_6H_5NH_2$) is formed. Aniline is a liquid, almost colorless when freshly prepared, but on long standing it turns to a dark-red color. Benzene has what is termed a *ring structure*, and this structure is characteristic of the coal-tar compounds in general. The structure of benzene, together with that of the derivatives nitrobenzene and aniline, is represented at the top of the following page.

benzene (C_6H_6)nitrobenzene ($C_6H_5NO_2$)aniline ($C_6H_5NH_2$)

Aniline is the compound from which many of the *aniline dyes* and *medicinal agents* are prepared. Thus, when aniline is heated with acetic acid, *acetanilide*, a well-known constituent of many headache powders, is formed according to the following equation:



2. **Toluene** ($C_6H_5-CH_3$). This is a liquid boiling at 110.5° and resembles benzene in its general properties. When oxidized, it forms *benzoic acid* (C_6H_5-COOH), the sodium salt of which (sodium benzoate) is a common food preservative. When treated with nitric acid, toluene forms the solid *trinitrotoluene* ($CH_3-C_6H_2(NO_2)_3$), commonly known as TNT. It constitutes an important explosive. From toluene there is also prepared the white solid known as *saccharin*, which is about 500 times as sweet as sugar. This was formerly used as a sweetening agent, but in 1912 the government forbade its further use in foods. It is used by diabetics, on prescription, to sweeten their food.

3. **Naphthalene** ($C_{10}H_8$). Ordinary moth balls are nearly pure naphthalene. This hydrocarbon was formerly used in making the well-known dye *indigo*; at present benzene has largely taken its place for this purpose.

4. **Anthracene** ($C_{14}H_{10}$). This hydrocarbon is used in the manufacture of *alizarin*, an important dye. This dye was formerly obtained from the root of the madder plant, which was grown in France on a large scale.

5. **Phenol (carbolic acid)** (C_6H_5-OH). This is a white crystalline solid, very corrosive and poisonous. It is the source material for the preparation of *salicylic acid*. It is also used in the manufacture of many plastics, such

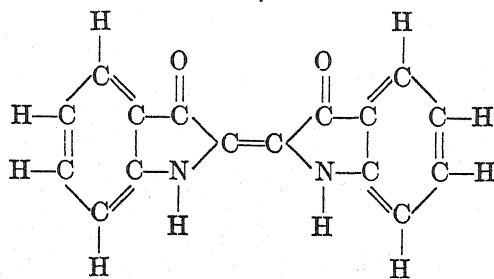
as *Bakelite*. When treated with nitric acid, phenol forms *picric acid* ($\text{C}_6\text{H}_2(\text{NO}_2)_3\text{OH}$), a yellow solid which is used as an explosive.

6. *Cresol (cresylic acid)* ($\text{CH}_3\text{—C}_6\text{H}_4\text{—OH}$). There are three isomeric cresols. A mixture of these is obtained directly from coal tar and constitutes the basis of most of the disinfectants now on the market.

Coal-tar dyes. All dyes prepared from compounds present in coal tar are known as *coal-tar dyes*, or *aniline dyes*. Many hundreds of these dyes have been prepared, of every imaginable color. Two of the most common of these, namely, *indigo* and *alizarin*, were formerly obtained from vegetable sources. Later, chemists found out how to make them in the laboratory, and now they are made in this way at a lower cost than they can be obtained from natural sources. The chemistry of dyeing will be discussed in a later chapter.

Previous to the war of 1914–1918 nearly all our dyes came from Germany. During the war this supply was cut off, and there was a temporary shortage of dyes. American chemists soon solved the problems connected with their production, and now the United States can produce an adequate supply of dyes of the highest grade.

Most of the aniline dyes are very complex compounds; for example, indigo has the following structural formula:



Historical. The first aniline dye was made in 1856 by an English boy seventeen years of age. His name was William Perkin. The boy was assisting in the laboratory of an English university, and during the holidays he spent his time in trying to make *quinine*. In the course of some experiments with aniline he noticed that a colored substance of great beauty was produced. Perkin got the idea that perhaps this new compound which he had prepared from aniline might be used as a dye. He finally succeeded in showing that it could be used, and that it was superior to vegetable dyes in coloring power. This discovery led to others; and the investigation continues, as shown by the fact that our dye factories employ hundreds of chemists. It is of interest to note that in 1906, fifty years after Perkin's discovery, he came to the United States and attended a great meeting held

in New York City in honor of the fiftieth anniversary of the discovery of the first aniline dye.

The chart (Fig. 305) gives us some idea of the kinds of compounds that are derived from coal tar, and also shows the relation of the compounds to each other. Thus, *toluene* is obtained directly from coal tar, as indicated by the arrow, while from toluene (following the arrows) we obtain benzoic acid, trinitrotoluene (TNT), saccharin, and Congo red. By simply following the arrows backward we can trace the *ancestry* of each compound named. Thus, the dyes at the bottom of the chart are all derived from aniline; but aniline is prepared from nitrobenzene, and this from benzene, which is obtained directly from coal tar.

Cause of certain transmissible diseases. The organisms known as protozoa and bacteria are the simplest forms of life, and each individual consists of a single cell. They may find their way into the human system through contaminated air, by infected food, or by contact infection, and are the cause of some of our most dreaded diseases. Many other diseases are due to what are called *filtrable viruses*. These will pass through a filter that will retain all microorganisms; they appear to be particles of some kind on the border line between living cells and large molecules of protein matter. It would seem reasonable to suppose that diseases caused by these organisms and viruses could be cured if we could find in nature or synthesize compounds that, introduced into the human body, would destroy the organisms and viruses without having any serious effect upon our bodies.

Historical. It has long been known that certain medicines are effective in curing different diseases. Thus the natives of South America, hundreds of years ago, discovered that there was some substance present in the bark of the cinchona tree that cured the dreaded malaria. Later investigations proved this substance to be the compound now known as *quinine*, and today we still obtain it from the same source and use it as our most effective drug for the cure of malaria.

As early as the year 1500, compounds of mercury were used in the treatment of syphilis, at times with some success, but generally with dire effect upon the patient's mouth, gums, and kidneys. Then about thirty years ago the German chemist Ehrlich, who was trying to synthesize some compound that would destroy the protozoa that caused the African sleeping sickness, made his 606th compound and found that it was a specific for syphilis. This compound, often called "606," contains arsenic; its chemical name is *arsphenamine*, and the trade name given it by Ehrlich is *Salvarsan*. Ehrlich also synthesized a related compound known as *Neosalvarsan*. This is not so potent as Salvarsan but is more easily administered.

New compounds for the cure of transmissible diseases. Ehrlich's success in finding a cure for syphilis led other chemists into similar fields of study. At first the progress was slow, but in 1935 very rapid progress began. The new compound known as *sulfanilamide* and its closely related compounds *prontosil* and *neoprontosil* were synthesized and found to be re-

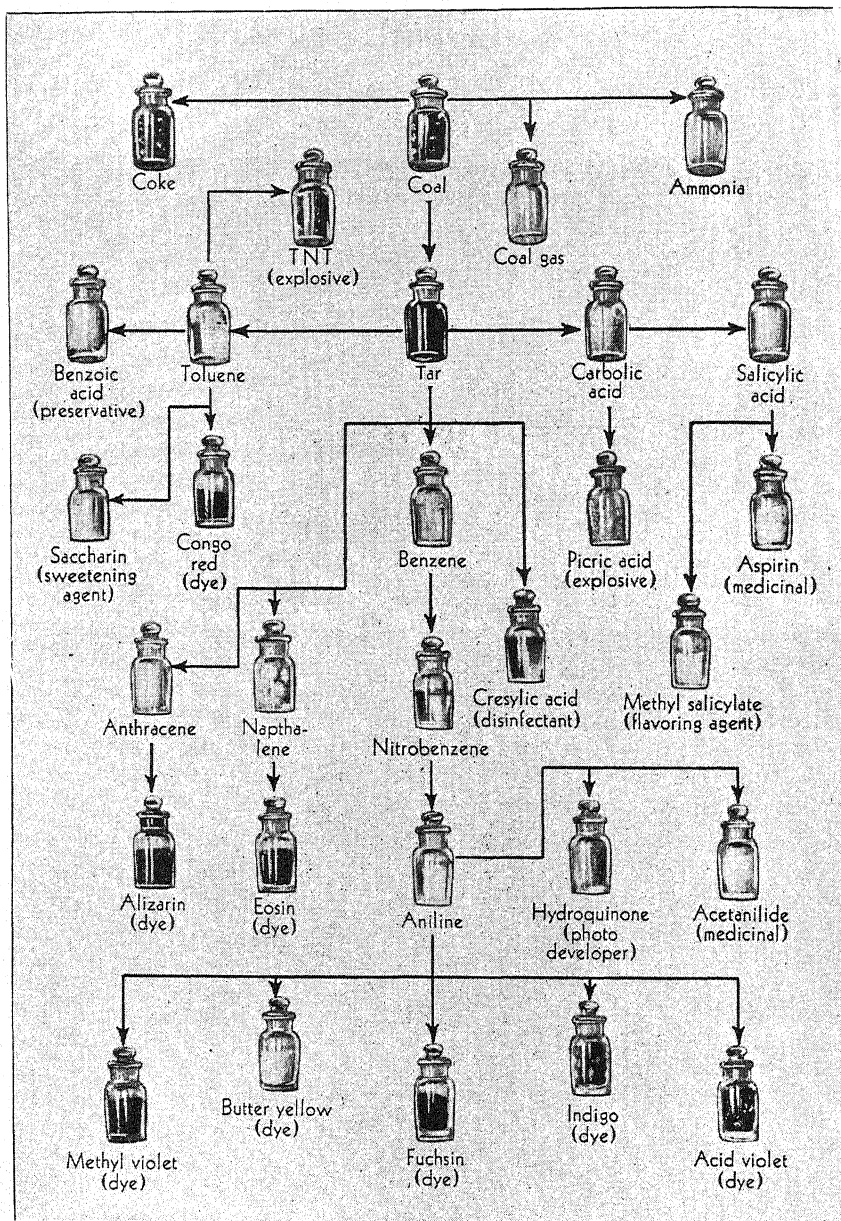
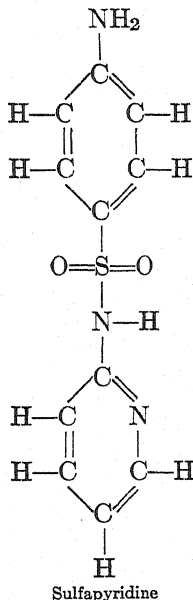
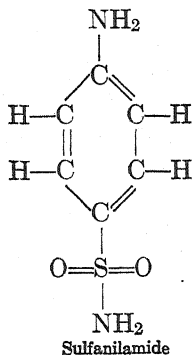


FIG. 305. Chart Showing the Source of a Few Important Coal-Tar Compounds

markably active in the cure of a number of our most virulent diseases, including meningitis, erysipelas, blood poisoning, and undulant fever (contracted from infected milk and meat). They also proved to be of some value in the treatment of our much-dreaded disease pneumonia.

Sulfapyridine is a compound prepared as the result of a deliberate effort to find a cure for pneumonia, and it proved to be much more effective than sulfanilamide for this purpose. It seems to yield good results in the case of all the thirty-two types of pneumonia now known and is completely effective for some.

Just how these compounds exert their effect is not known. The structural formulas for the two most important are given below.



Chemotherapy. Many chemists are busy synthesizing new compounds not only to fight infections but to relieve pain (anodynes), to induce sleep (soporifics), and to furnish the chemical substances normally secreted by healthy glands (hormones). Once promising products are obtained, as proved by tests on mice and guinea pigs and finally on human beings, the chemist alters the architecture of his molecule, changing atoms and groups here and there, in an effort to achieve an even greater chemical potency with less harm and shock to the patient. This branch of chemistry is known as *chemotherapy* (cure by chemicals).

Questions

1. What distinction do you make between the following terms : (a) *isomeric* ; (b) *polymeric* ; (c) *allotropic* ?
2. (a) Could cotton wool be converted into a sugar ? (b) Would it be a food ?
3. Could rayon be made in any industrial country ?
4. There are two isomeric butyl alcohols, C_4H_9OH . Can you suggest structural formulas to show a difference between them ?
5. (a) Could methyl alcohol be made by starting with water gas (and so indirectly from coal and water) ? (b) By what reaction could ethyl alcohol be prepared by starting with ethylene ?
6. Proposals have been made to require the addition of alcohol to gasoline as an aid to farmers. (a) How could this be an aid ? (b) Do you see any difficulties in such a plan ?
7. Suppose that each of the following compounds is in the vapor state. What volume changes result from its combustion ? (a) Methyl alcohol ; (b) ethyl alcohol ; (c) ethyl ether ; (d) benzene.
8. (a) What enzymes can you name ? (b) What change does each produce ?
9. Write the equations for the reactions that take place in preparing aniline from benzene.
10. (a) What is the maximum percentage of alcohol that can be obtained in aqueous solution by direct fermentation of sugar ? (b) If enough sugar is present, why will not a larger percentage result ?
11. The Federal statutes permit the use of a preservative (sodium benzoate) in tomato catchup but not in milk. Why ?
12. Do you think our laws should permit foods to be artificially colored ?

Problems

1. Calculate the percentage composition of starch.
2. Assume that 80 per cent of cellulose can be converted into ethyl alcohol. What weight of cellulose would be required for the preparation of 100 l of absolute alcohol (temperature 20°) ?
3. Assuming the yield to be 100 per cent, find the weight of formalin that can be prepared from 1 kg of pure methyl alcohol.
4. Write the equations for the reactions that take place in the preparation of acetanilide. If 100 per cent yields are assumed, what weight of acetanilide can be prepared from 100 kg of benzene ?

5. What weight of aniline can be prepared from 100 g of benzene?
6. What is the percentage loss in weight in the conversion of alcohol into ether?

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Organic Acids; Fats and Oils; Foods

Organic acids. Among the compounds of carbon are included a number of acids which are present in certain organisms or the products derived from them. Thus, *citric acid* is present in lemons and grapefruit, *lactic acid* in sour milk, and *acetic acid* in vinegar. Collectively all such acids are known as the *organic acids*. Many of them occur in nature either as the free acid or as some derivative of the acid. The most common of these acids contain the elements hydrogen, carbon, and oxygen; and the oxygen atoms are arranged

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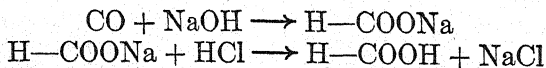
in a grouping called the *carboxyl* group, —C—OH , sometimes written simply —COOH . It is the hydrogen atom in this group which is replaceable by metals and is therefore the *acid hydrogen*. An acid containing but one —COOH group is monobasic, while one containing two such groups is dibasic. Like the hydrocarbons, the acids can be arranged in series. Of these one of the most important is known as the *fatty acid series*, since some of the higher members of the series are obtained from natural fats.

The fatty acid series. A few of the most important members of this series are the following:

H—COOH	formic acid, a liquid boiling at 100.5°
$\text{CH}_3\text{—COOH}$	acetic acid, a liquid boiling at 118.1°
$\text{C}_3\text{H}_7\text{—COOH}$	butyric acid, a liquid boiling at 163.5°
$\text{C}_{15}\text{H}_{31}\text{—COOH}$	palmitic acid, a solid melting at 64°
$\text{C}_{17}\text{H}_{35}\text{—COOH}$	stearic acid, a solid melting at 69.3°
$\text{C}_n\text{H}_{2n+1}\text{—COOH}$	general formula, n being the number of carbon atoms

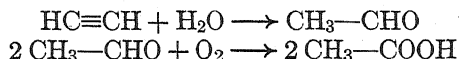
Formic acid (H—COOH). This is a colorless liquid and occurs in many plants, such as the stinging nettle. It is also present in a certain species of ant (the word *formic* is derived from a Latin word meaning "ant"). It is a strong acid — much stronger than acetic acid. It is used for the preparation of carbon monoxide (p. 457).

Formic acid is prepared on a large scale by heating carbon monoxide and sodium hydroxide under pressure, and then treating the sodium formate with hydrochloric acid:

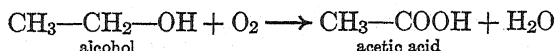


Acetic acid ($\text{CH}_3\text{—COOH}$). This is the acid which gives the sour taste to vinegar. It is prepared commercially by the distillation of wood (p. 454), as well as by the oxidation of dilute alcohol. It is a colorless liquid and has a strong, pungent odor. When anhydrous, it crystallizes as a white solid which melts at 16.6° and closely resembles ice in appearance; hence the name *glacial* acetic acid. Many of the salts of acetic acid are well-known compounds; for example, lead acetate ($(\text{CH}_3\text{—COO})_2\text{Pb} \cdot 3 \text{H}_2\text{O}$) is a white salt called *sugar of lead*.

Just as synthetic methyl alcohol (p. 507) threatens to displace that obtained by distilling wood, so synthetic acetic acid is now being produced in quantities. The process consists in combining acetylene with water through the catalytic action of mercuric sulfate, forming acetaldehyde ($\text{CH}_3\text{—CHO}$). The aldehyde is then easily oxidized to acetic acid:



Vinegar. As is well known, when cider is exposed to the air, it is gradually transformed into vinegar. Two changes are involved in the process: (1) the sugar in the cider first undergoes alcoholic fermentation, forming *hard cider*, which contains from 4 to 8 per cent of alcohol; (2) the alcohol is then oxidized to acetic acid by the oxygen of the air. This oxidation is brought about by certain bacteria, and is called *acetic fermentation*. It may be represented as follows:



The manufacture of vinegar. The rate of acetic fermentation may be greatly increased by providing intimate contact between the alcohol solution and the oxygen of the air. This may best be accomplished by loosely filling a large cask (*generator*) with beech shavings, spraying vinegar into the top of the cask to introduce the bacteria, and then similarly spraying a dilute solution of alcohol (*hard cider*, in the case of cider vinegar) while admitting air at the bottom. The resulting vinegar is drawn off at the bottom of the cask.

Instead of starting with cider, one may use almost any substance which contains starch or sugar; for these compounds change into alcohol, as explained in the manufacture of alcohol. In this way *malt vinegar* is prepared from starch and *sugar vinegar* from sugar residues. The cheapest vinegar is made from pure dilute alcohol and is known as *distilled vinegar*. It is colorless and leaves almost no residue upon evaporation.

A Federal law requires that all vinegar shall contain not less than 4 per cent acetic acid. Vinegar prepared from fruits and grains contains certain

solids derived from the source materials. It is by studying the character of these solids left upon evaporating a sample of vinegar that the chemist is able to determine the source of the vinegar.

Butyric acid (C_3H_7-COOH). Butyric acid is a liquid of disagreeable odor. Derivatives of the acid are present in butter and give it its characteristic taste.

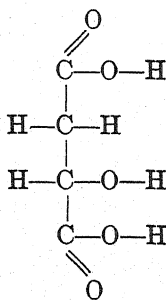
Palmitic acid ($C_{15}H_{31}-COOH$) and stearic acid ($C_{17}H_{35}-COOH$). These are white solids insoluble in water. They are obtained from fats.

Acids belonging to other series. In addition to the members of the series described above, mention may be made of the following well-known acids, the first four of which are white solids:

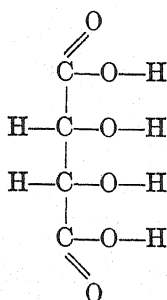
1. **Oxalic acid ($HOOC-COOH$).** Salts of this acid are found in many plants, especially in sorrel and rhubarb. It is one of the products of oxidation of sucrose, and is prepared commercially by heating cellulose products such as sawdust with concentrated solutions of the hydroxides of potassium and sodium. The acid is used in dyeing and in bleaching straw goods.

2. **Malic acid ($HOOC-CH_2-CHOH-COOH$).** Malic acid occurs in a free state in apples, pears, and other fruits, as well as in the berries of the mountain ash.

3. **Tartaric acid ($HOOC-CHOH-CHOH-COOH$), or ($C_4H_6O_6$).** Because this acid is dibasic, its molecular formula is sometimes written $H_2 \cdot C_4H_4O_6$. It occurs in many fruits, especially the grape, either in a free state or in the form of its salts. Some of its salts are well-known compounds. Potassium acid tartrate ($KHC_4H_4O_6$), ordinarily known as *cream of tartar*, is a white solid obtained from grape juice and is used in the manufacture of some baking powders. Potassium sodium tartrate ($KNaC_4H_4O_6 \cdot 4 H_2O$) is used in medicine under the name *Rochelle salt*. The free acid is a common constituent of "pop" and other soft drinks.



Structural Formula of Malic Acid

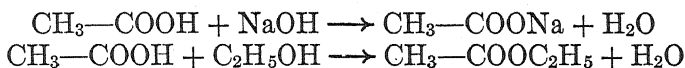


Structural Formula of Tartaric Acid

4. *Citric acid* ($C_3H_4(OH)(COOH)_3$). This acid (tribasic) occurs in the citrus fruits, such as the lemon and grapefruit. It is a white solid soluble in water. Its magnesium salt is a common medicine.

5. *Oleic acid* ($C_{17}H_{33}-COOH$). The derivatives of this acid constitute the principal part of many oils and liquid fats. The acid itself is an oily liquid. The molecule of oleic acid has two hydrogen atoms less than stearic acid (p. 522). In the oleic acid molecule there is a double bond between two of the carbon atoms along the carbon chain.

Esters (ethereal salts). Acids seem to act on alcohols in much the same way as on bases, although less energetically. This similarity of action is shown in the following equations, which represent the reactions taking place when acetic acid acts on sodium hydroxide and ethyl alcohol respectively:



The compounds formed by the action of an acid on an alcohol, of which *ethyl acetate* ($CH_3-COOC_2H_5$) may be taken as a typical example, are called *esters*, or *ethereal salts*. They differ in composition from ordinary salts in that they contain a hydrocarbon radical in place of a metal. The esters are largely used as solvents, especially in the cellulose nitrate industries.

When an ester is heated with a strong base, a salt and an alcohol result, as illustrated in the following equation:

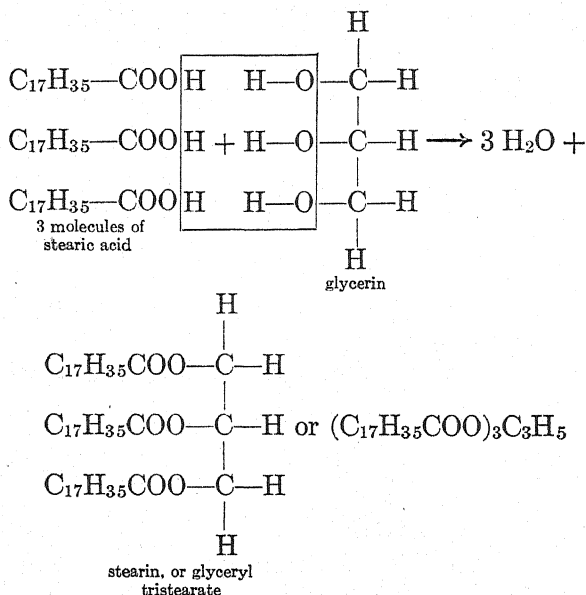


This reaction between an ester and a metallic base, which results in the formation of a salt and an alcohol, is called *saponification*. As we shall see, it is the reaction which takes place in making soap.

Oils and fats derived from animal and vegetable sources. The various oils obtained from petroleum are called *mineral oils* (p. 469). There are a great many other oils and fats, such as olive oil, lard, and butter, that are derived from *vegetable* and *animal* sources. These two classes of oils, the mineral oils and those derived from vegetable and animal sources, are entirely different in composition and chemical conduct. The mineral oils are hydrocarbons; the animal and vegetable oils are composed mainly of mixtures of three esters known as *olein*, *palmitin*, and *stearin*. Olein is a thick, colorless liquid and is the principal constituent of the vegetable oils, such as olive oil and cottonseed oil. Palmitin and stearin are white solids

and constitute the greater part of solid fats, such as tallow. In addition to these three constituents the vegetable and animal oils contain small percentages of other compounds, derived from the source material, and it is these compounds that give to each oil and fat its individual characteristics.

Composition of palmitin, stearin, and olein. These three compounds are all esters and may be regarded as derived from palmitic, stearic, and oleic acids, respectively, and glycerin (often called glycerol). The molecule of glycerin (which is an alcohol) contains three hydroxyl groups ($-\text{OH}$), each one of which will react with a separate acid molecule in ester formation :



The residue group, C_3H_5 , left when the three OH groups are removed from a glycerin molecule, is called a *glyceryl* radical, since it is the radical present in glycerin, $\text{C}_3\text{H}_5(\text{OH})_3$. Similarly, olein is glyceryl trioleate, $(\text{C}_{17}\text{H}_{33}-\text{COO})_3\text{C}_3\text{H}_5$, and palmitin is glyceryl tripalmitate, $(\text{C}_{15}\text{H}_{31}-\text{COO})_3\text{C}_3\text{H}_5$.

Butter fat and oleomargarine. While butter fat, like other fats, consists principally of olein, palmitin, and stearin, its characteristic flavor is due to the presence of small quantities of other esters present in milk. *Oleomargarine* differs from butter mainly in the fact that

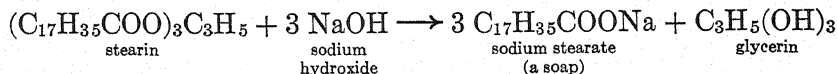
a smaller percentage of the esters characteristic of butter is present. It is made from the fats obtained from cattle and hogs. Often vegetable oils, such as coconut oil and cottonseed oil, are used. These fats are churned with milk or mixed with a small quantity of butter in order to give the butter flavor.

In appearance oleomargarine differs from most butter in being nearly colorless. While it is a common practice to color butter artificially, the Federal law permits the coloring of oleomargarine only upon the payment of a tax of 10 cents for each pound colored. Many of the states, however, have laws forbidding the sale of oleomargarine that is artificially colored, even though the Federal tax has been paid.

The hydrogenation of fats; changing oils into solid fats. Stearin differs from olein in composition in that it contains six more atoms of hydrogen in each molecule (since a single molecule of stearic acid contains two more hydrogen atoms than a molecule of oleic acid). Now, if hydrogen is brought in contact with olein under proper conditions and in the presence of a suitable catalyst (finely divided nickel is used), the olein takes up the additional hydrogen and is changed into the solid stearin. This process is called the *hydrogenation of fats*. It is possible in this way to change the oils into solid or semisolid fats which are better adapted for use as foods and for making soaps and candles.

Soaps. Soaps are made by heating some fat or oil with an aqueous solution of sodium hydroxide or potassium hydroxide. The fats and oils commonly used are low-grade animal fats (tallow and grease) and the cheaper vegetable oils, such as palm oil and coconut oil. Sodium hydroxide gives a hard soap and on this account is used in preference to potassium hydroxide, which gives a soft soap. Since the fats and oils are composed of esters, the process of soapmaking is one of *saponification*, and the fat is said to be *saponified*.

Remembering that fats and oils consist mainly of olein, palmitin, and stearin, we may illustrate the reactions that take place when these are heated with sodium hydroxide by the following equation, which represents the change in the case of stearin :



The products of the reaction, then, consist chiefly of glycerin and a mixture of sodium oleate, sodium palmitate, and sodium stearate. These sodium salts, separated from the glycerin formed along with them, make up the main constituents of all ordinary soaps.

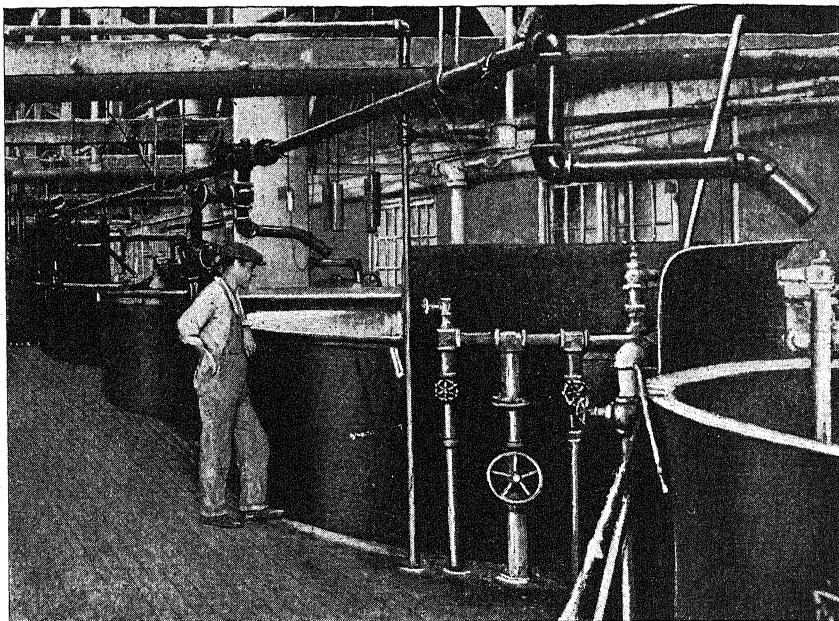


FIG. 306. *The Manufacture of Soap*

The melted fat or oil, mixed with a solution of sodium hydroxide, is heated in large iron kettles

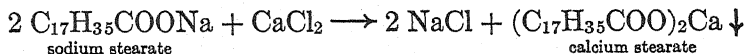
The reactions in soapmaking are carried out in large kettles heated by steam (Fig. 306). Over 500,000 pounds of soap are often made in a single heating. When the reaction is complete, the soap is in the form of a colloidal dispersion in the liquid present. In order to coagulate the soap, sodium chloride is added (p. 442) — a process known as "salting out." The soap so obtained is purified by washing and is then run into a mixing machine (crutcher). Here it is mixed with any appropriate material desired, such as perfume, borax, sodium silicate, or sodium carbonate. It is then run into large molds, called *frames*, to harden, after which it is cut and pressed into cakes of the desired size. The glycerin formed in the reaction is concentrated by evaporation and refined by distillation.

Varieties of soap. Transparent soaps are ordinarily made by dissolving the dried soap in alcohol and distilling off the excess alcohol. The resulting product is set aside until the insoluble impurities settle out. The solution, separated from the impurities, is solidified by chilling. The solid soap is then cut and stamped into cakes. On long standing these lose all their alcohol and water and become transparent. Floating soaps owe their lightness to bubbles of air. Naphtha soaps contain a small percentage of petroleum naphtha. Scouring soaps contain from 5 to 10 per cent of soap and from 80 to 90 per cent of some abrasive material, such as fine sand or vol-

canic ash. Sometimes a small percentage of sodium carbonate is also present. Soap powders are, as a rule, normal sodium phosphate or sodium carbonate mixed with from 10 to 25 per cent of ground soap.

Other new detergents have valuable properties. For example, the long-chain sulfates, $\text{CH}_3(\text{CH}_2)_n\text{—OSO}_3\text{Na}$, where n is 10 or greater, act like soap in hard as well as in soft water, and are effective in acid waters which would precipitate the fatty acids from ordinary soaps.

Properties of soap. When soap is added to soft water, it apparently dissolves. Experiments show, however, that some of the soap is present in the form of a colloidal dispersion (or sol). Some hydrolysis takes place, so that the liquid is basic in character. The calcium and magnesium salts of oleic, palmitic, and stearic acids are insoluble in water and do not form emulsions, so that they are precipitated when a calcium or magnesium compound is added to an aqueous solution of soap:



It is due to this fact that soaps do not lather with hard waters but form a curdy precipitate, since such waters always contain salts of calcium and magnesium in solution.

Cleansing action of soap. There has been a great deal of study and discussion in the effort to find out the true explanation of the cleansing action of soap, and much uncertainty still remains. Attention has been called (p. 444) to the property possessed by soap of aiding in the formation of emulsions, and the cleansing action of soap is thought to be due primarily to this property (Fig. 307). When soap is rubbed on the skin, any fatty substances present are emulsified by the soap and washed away. Another factor in the cleansing action of soap is the low surface tension of soap solutions, which makes them spread readily over surfaces and penetrate into minute openings.

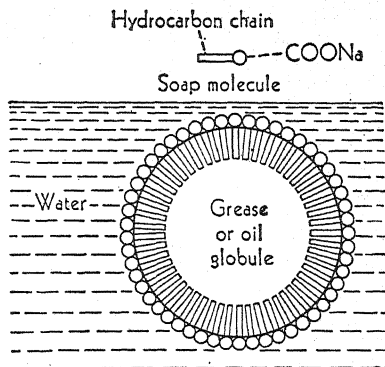
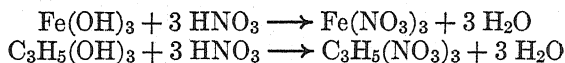


FIG. 307. *The Cleansing Action of Soap*

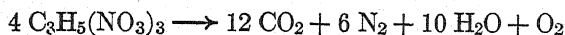
According to one plausible theory globules of grease or oil are emulsified by being coated completely with a film of soap molecules. The hydrocarbon chains of the soap molecules dissolve in the oily globules, and the —COONa groups place themselves outside, in contact with the water

Glycerin (glycerol) ($C_3H_5(OH)_3$). This compound, as already stated, is really an alcohol, for it may be regarded as derived from the hydrocarbon *propane* (C_3H_8) by displacing three atoms of hydrogen, on the three different carbon atoms, by three hydroxyl groups. We have seen that it is formed in the process of making soap; indeed, every soap factory is likewise a glycerin plant. It is also formed in small amounts in alcoholic fermentation (p. 508). By carefully regulating conditions this amount can be increased to as much as 35 per cent of the sugar fermented. It can also be synthesized from propylene (C_3H_6), a hydrocarbon formed in the cracking of petroleum. Glycerin is an oily, colorless liquid and, as the name suggests, has a sweetish taste. Its chief use is in the manufacture of *glyceryl nitrate*.

Glyceryl nitrate and dynamite. Nitric acid reacts with glycerin in the same way as it reacts with a base containing three hydroxyl groups, such as $Fe(OH)_3$:



The resulting nitrate, $C_3H_5(NO_3)_3$, is the main constituent of *glyceryl nitrate* (commonly known as *nitroglycerin*), and is a slightly yellowish, very explosive oil. It explodes by pressure, by detonation, or by heating to 250° . The following equation represents in a general way the changes which take place in the decomposition of the nitrate:

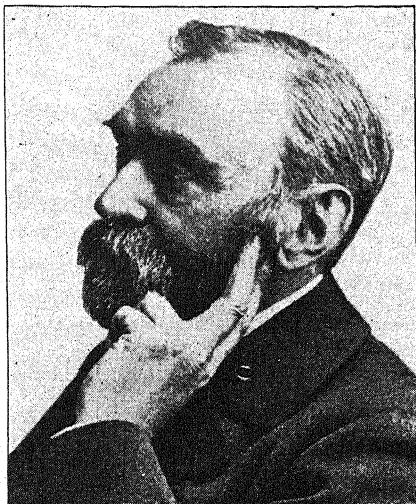


One volume of *glyceryl nitrate* on explosion yields about 1300 volumes of gaseous compounds, which are expanded by the heat of decomposition to over 10,000 volumes. *Dynamite* consists of a mixture of sodium nitrate or ammonium nitrate, wood pulp, and *glyceryl nitrate*. The wood pulp acts as an absorbent for the *glyceryl nitrate*. The strength of the dynamite depends primarily on the percentage of *glyceryl nitrate* present. *Dynamite* is used much more than *glyceryl nitrate*, since it does not explode so readily and can be transported with safety.

Historical. Nitroglycerin was first prepared by the Italian Sobrero, but it was not considered usable as an explosive because of its liquid state and poisonous qualities. In 1862 the young Swede Alfred Nobel (Fig. 308) determined to manufacture this "blasting oil," though he had to place his factory on a barge and move it about as protests against its presence arose.

By a chance leak in a can of nitroglycerin he noticed that the infusorial earth in which the can had been packed had absorbed the liquid nitroglycerin to make a thick paste. He found this paste to be less readily explosive than liquid nitroglycerin and safer to handle. This was the first dynamite, patented in 1867.

Nobel devoted his life to perfecting a number of high explosives and died a wealthy man. He dedicated his fortune to the causes of universal peace and science. The Nobel Foundation, established in Stockholm in 1900, provides yearly awards of about \$40,000 value each to those five persons who, during the preceding year, have contributed most materially to human advancement in the fields of physics, chemistry, physiology and medicine, literature, and peace. At the discretion of the awarding committees in any given year, any of these prizes may be awarded jointly to two or more persons or may be withheld entirely.



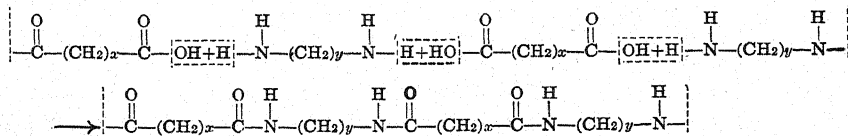
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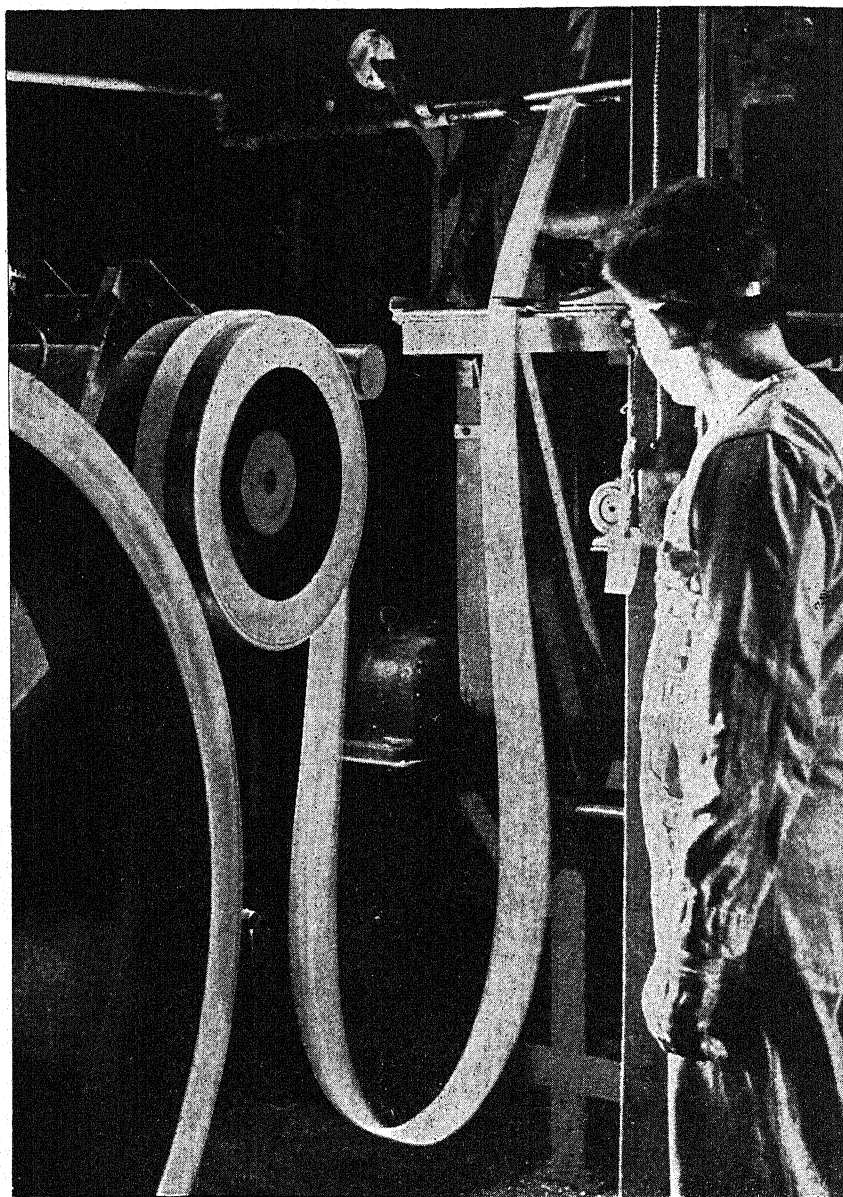
FIG. 308. *Alfred Bernhard Nobel*
(1833-1896)

Distinguished Swedish inventor, and
founder of the Nobel prizes

Glycol ($C_2H_4(OH)_2$). If we displace one hydrogen atom in ethane (C_2H_6) by a hydroxyl radical, we obtain ordinary alcohol (C_2H_5OH). If we displace two, one from each carbon atom, then we obtain the compound $C_2H_4(OH)_2$, or $(HO-CH_2-CH_2-OH)$, known as *ethylene glycol*, or simply *glycol*. This compound is a colorless liquid and boils at 197.5° . It is the compound sold under the trade name *Prestone*, as an antifreeze for filling automobile radiators in cold weather. Glycol nitrate, $C_2H_4(NO_3)_2$, resembles glyceryl nitrate very closely and possesses the desirable characteristic of not freezing in cold weather.

Nylon. In recent years Stine, Carothers, and their colleagues, working in the research laboratories of the Du Pont Company, found that molecules of the straight-chain dibasic acids $(HOOC-(CH_2)_x-COOH)$ and the straight-chain diamines $(H_2N-(CH_2)_y-NH_2)$ will join hands, so to speak, by splitting off water as shown in the equations below, thus forming long molecules containing a large number of each of these units:





E. I. du Pont de Nemours and Company

FIG. 309. *One Step in the Manufacture of Nylon*

The picture shows a ribbon of molten Nylon being extruded from the vessel in which the Nylon is prepared

The resulting material has been given the trade name of *Nylon*. Since there are many dibasic acids and diamines, many different

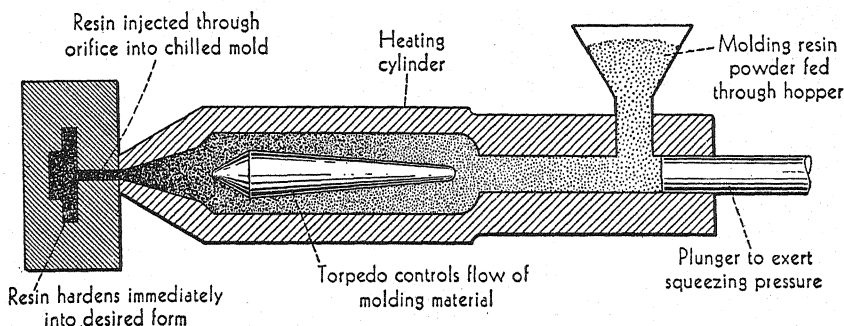


FIG. 310. A Cross Section of a Device for Molding Plastics by Pressure

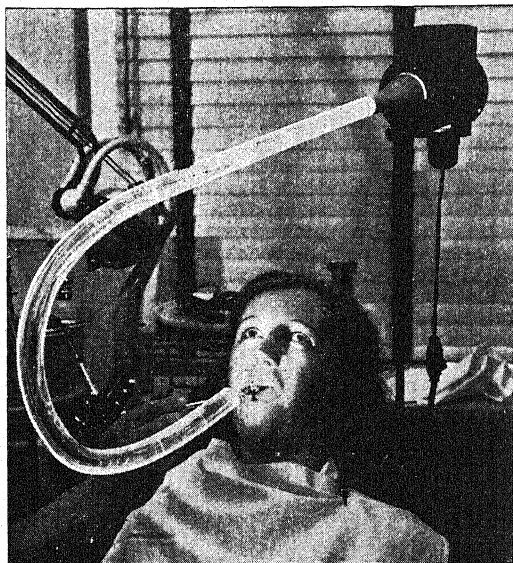
forms of Nylon are possible. These are all solid, protein-like compounds, which can be melted and pushed through tiny holes to form continuous, fine threads in much the same way that a spider forms the filaments of its web (see rayon filaments, Fig. 302).

The Nylon yarn made from the fine threads is similar in composition to silk, to which it bears a remarkable resemblance. It is also stronger and more elastic than silk, wool, linen, cotton, and rayon. Commercial production of Nylon began in 1940 (Fig. 309), and the product, woven into cloth or hosiery, promises to replace, at least partly, the more expensive and less durable natural silk. Also, melted Nylon is used to make excellent bristles for many kinds of brushes and to fabricate hundreds of useful and decorative articles.

Plastics (resins). The word *plastic*, or *resin*, is applied to substances that can be molded into some desired shape. In its broadest sense, this definition would include such materials as iron and glass; but the words are commonly restricted to products obtained from plants and trees, and to the much larger number now prepared in the laboratory. The latter are made by first causing relatively simple compounds to unite, and then polymerizing the product into still more complex bodies. Slosson compared the process of their formation to a molecular trust formed by the merger of a large number of relatively small molecules.

Most of the plastics are waterproof and can be softened by heat and easily molded by pressure (Fig. 310). The plastics industry, already an immense one, is still rapidly expanding and is claiming many fields in which wood, metals, glass, and other materials of fabrication were formerly employed.

Some important synthetic resins. 1. *Bakelite*. The first important synthetic resin was made by the American chemist Baekeland, and named *Bakelite*. It is



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FIG. 311. One Way in Which Dentists Use Lucite

the product of the reaction between phenol and formaldehyde, and has countless uses, since it is adapted to making certain automobile parts, electrical instruments, telephone receivers, camera cases, pipstems, buttons, handles for umbrellas, brushes, and cooking utensils, and similar articles.

2. *The acryloid resins*. These are made by the polymerization of the methyl ester of either acrylic acid ($\text{H}_2\text{C}=\text{CH}-\text{COOH}$) or

methyl acrylic acid. The resin prepared from the latter is called *Lucite*. This is a crystal-clear solid which has the optical properties of glass and can be molded, or cut with a saw or knife, or tooled in a lathe. An interesting property of Lucite is that light will pass along within a rod made of it as if through a tube, even though the rod be bent (Fig. 311). The acryloid resins are molded cheaply into lenses and prisms, as well as sheets and rods and other useful forms.

3. *Phthalic acid resins*. Another interesting group of resins is made by the polymerization of the compound prepared by the action of phthalic acid ($\text{HOOC}-\text{C}_6\text{H}_4-\text{COOH}$) on either glycerin or glycol. Water splits off between the COOH groups of the acid and the OH groups of these two alcohols, and the resulting compound polymerizes, forming long threads.

Further resins are prepared from urea (p. 462), styrene ($\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$), and compounds containing the vinyl radical ($\text{CH}_2=\text{CH}-$).

FOODS

Composition of foods. While the compounds present in our foods are very numerous, and often exceedingly complex in structure, they may all be included in one or more of the following general classes:

1. **Proteins.** This term is applied to a large class of complex nitrogenous compounds which are everywhere abundant in animal and vegetable organisms, and which constitute the principal part of the tissues of the living cell. The *casein* of milk, the *gluten* of flour, and the *albumin* of egg are proteins. All the proteins contain nitrogen, carbon, hydrogen, and oxygen, and some also contain sulfur and phosphorus. Very small percentages of other elements are present in certain proteins; thus, hemoglobin, which is present in blood, contains iron.

2. **Fats.** These consist of a mixture of the glyceryl esters of certain acids (p. 524).

3. **Carbohydrates.** This group includes the sugars, starches, and related compounds.

4. **Mineral matter.** Certain compounds of the metals, such as calcium phosphate, are also present. Since these compounds, or others formed when they are heated, are left as a residue when the food is burned, they are listed as *ash* in reporting the analysis of foods.

5. **Water and oxygen.** While we do not usually speak of water and oxygen as foods, nevertheless both are essential to life, and they deserve to be called foods in the true sense of the word.

6. **Vitamins.** For a long while it was thought that the only substances necessary for the growth of the body and the preservation of health were those listed above. It was found, however, that animals could not maintain their health if fed on perfectly pure proteins, fats, and carbohydrates. Further experiments to find the reason for this proved that many of our foods contain very small percentages of complex substances, to which the name *vitamins* has been given, and that these vitamins are absolutely essential to health.

Partly because the vitamins are present in such small percentages, and partly because they are very complex and difficult to purify, our knowledge of them is incomplete and often contradictory. In brief, the function and some of the most potent sources of vitamins are as follows:

Vitamin A. This vitamin has been obtained in pure crystalline form ($C_{20}H_{30}O$) from certain fish oils, as well as from carotene — a compound present in carrots and some other vegetables. Either the vitamin itself or carotene, which yields the vitamin in the process of metabolism, is present in

many foods, especially in all milk and dairy products, cod-liver and halibut-liver oils, and green-leaf vegetables, such as spinach and turnip-greens. It functions to promote growth, to maintain resistance to infections, and to correct certain eye troubles. It is also essential to maintain the normal conditions of the mucous membranes of the respiratory and digestive tracts.

Vitamin B. When first discovered, this vitamin was thought to be a single compound, but later investigations proved it to consist of at least eight or ten compounds. B_1 (thiamin, $C_{12}H_{16}N_4OS$) has been synthesized and is a commercial product. It is the antineuritic vitamin, preventing neuritis; it also promotes growth and stimulates the appetite. Good sources of this vitamin are yeast, whole-wheat bread, and most vegetables. B_2 , sometimes called vitamin G, or riboflavin ($C_{17}H_{20}N_4O_6$), is a commercial synthetic product. It also promotes growth and improves health. Another of the B vitamins is nicotinic acid ($C_6H_5O_2N$), also called niacin, and it is a commercial product. It prevents the disease known as pellagra. B_6 (adermin, $C_8H_{11}NO_3$) maintains the normal health of the skin.

Vitamin C. This vitamin consists of an acid known as ascorbic acid ($C_6H_8O_6$). It has been synthesized and is sold by druggists as a preventive of the disease known as scurvy. Citrus fruits (especially orange juice), raw cabbage, and tomatoes are some of the best sources of this vitamin.

Vitamin D. As with vitamin B, there are a number of forms of this vitamin, all similar in structure and properties. It prevents rickets and other bone diseases especially prevalent among children. Cod-liver and halibut-liver oils are good sources of the vitamin; also foods that contain the fat known as ergosterol, after these foods have been exposed to ultra-violet rays (Fig. 104). These rays convert the ergosterol into vitamin D. Exposure of our bodies to the sun has a similar effect, since the rays change the ergosterol present in the skin into vitamin D.

Vitamin E. This vitamin has been synthesized ($C_{29}H_{50}O_2$) but is not a commercial product. It is present in vegetable oils (especially in the oil of wheat germs), lettuce, and meats. It is necessary for reproduction and the growth of young animals before birth.

Vitamin G. This is one of the forms of vitamin B.

Vitamin K. This more recently discovered vitamin helps to prevent hemorrhage. It has been synthesized and is a commercial product. Cabbage, tomatoes, many green vegetables, and egg yolk, all contain it.

Just how the vitamins act to promote growth and prevent many diseases is not known. A diet made up chiefly of milk and other dairy products, green vegetables, grains, fruits, and some meats will furnish our bodies with an adequate supply of all the known vitamins.

Dietetic value of some foods. The following table, which has been taken from Bulletin No. 28, office of the Experiment Station,

Washington, D.C., gives the average composition of the edible portion of a few typical foods, expressed in grams per 100 grams of food :

KIND OF FOOD	WATER	PROTEIN	FAT	CARBO- HYDRATES	ASH	FUEL VALUE IN KILOGRAM- CALORIES
Apples	84.6	0.4	0.5	14.2	0.3	63
Beans (dried)	12.6	22.5	1.8	59.6	3.5	345
Beef (slightly fat) . .	73.8	22.1	2.9	—	1.2	115
Bread (white)	35.3	9.2	1.3	53.1	1.1	260
Butter	11.0	1.0	85.0	—	3.0	769
Corn (green)	75.4	3.1	1.1	19.7	0.7	101
Eggs	73.7	14.8	10.5	—	1.0	154
Ham (lean, smoked) .	53.5	20.2	20.8	—	5.5	268
Lettuce	94.7	1.2	0.3	2.0	0.9	16
Milk	87.0	3.3	4.0	5.0	0.7	69
Oatmeal	7.3	16.1	7.2	67.5	1.9	400
Olive oil	—	—	100.0	—	—	900
Oranges	86.9	0.8	0.2	11.6	0.5	51
Peas (green)	74.6	7.0	0.5	16.9	1.0	100
Potatoes	78.3	2.2	0.1	18.4	1.0	83
Rice	12.3	8.0	0.3	79.0	0.4	351
Spinach	92.3	2.1	0.3	3.2	2.1	200
Tomatoes	94.3	0.9	0.4	3.9	0.5	23
Wheat flour	11.9	13.3	1.5	72.7	0.6	357

Functions of the different classes of food materials. In general it may be stated that the protein matter in our food serves to replace the worn-out organic tissues of our bodies, as well as to supply material for growth. The fats and carbohydrates are more or less interchangeable, since both are oxidized in the body and are a source of heat and muscular energy. The mineral matter supplies the material for building up the solid structure of the body, and has in addition other complex functions. The protein matter may fulfill the function of the fats and carbohydrates to a certain extent, in case the latter are lacking in our foods. Since the various constituents of our foods serve different purposes, it is evident that a proper mixture of all is essential to the health of the individual. They should, of course, be sought in a palatable and digestible form. Some foods, such as milk, may not seem to rank high as an economical food considered simply from their content of fat, carbohydrate, and protein; yet when we take into account the character of the constituents present, and especially their vitamin and mineral content, their effect on maintaining health may make them very valuable.

Calorific value of foods. One of the important functions of food is to supply the energy expended by the body. Apart from mineral salts and water most of the constituents of our foods when digested undergo oxidation in the body, the carbon and hydrogen being in large part oxidized to carbon dioxide and water. The heat of the body is due to this oxidation. The chief function of a considerable portion of our food is to maintain this supply of energy; so the *calorific value* (p. 486) of foods is a matter of much importance.

On the average the calorific values of the three principal groups of foodstuffs, as determined in the calorimeter and in actual combustion within the body, are as follows (1 Cal = 1000 cal) :

CLASS OF FOODS	CALORIES PER GRAM	CALORIES PER POUND
Carbohydrates	4	1815
Fats	9	4082
Proteins	4	1815

Food requirements from the standpoint of calorific value. Naturally these requirements vary with conditions, such as one's age, occupation, and the climate in which one lives. Different standards have been proposed, but the following are generally accepted as normal :

1. *The twenty-four-hour protein requirement in grams per kilogram of body weight.* This requirement is proportionally greater in the growing child than in adults. For children from one to three years, the intake should be about 3.5 g, gradually diminishing to 1 g for adults of twenty-one years of age and upward.

2. *The twenty-four-hour Calorie requirements.* For an adult living an ordinary life in a temperate climate, and not engaged in manual work, 2400 Cal are sufficient. If one is engaged in muscular work, there should be added to this from 75 to 300 Cal per hour of work, depending upon how much work is done. Children require proportionally less, beginning with about 840 Cal at one year of age and gradually increasing to 2400 at fifteen years of age.

In stating food requirements for a period of, say, twenty-four hours it is necessary only to give the weight of protein needed, together with the total fuel value; for the fats and carbohydrates have nearly the same function. The difference between the total fuel value and the value of the needed protein gives the number of Calories to be supplied from fats and carbohydrates. A mixture of these two food materials is selected such that its fuel value, together with the fuel value of the protein, equals the total fuel value required.

Questions

1. Give the names and formulas of five important organic acids; also the name and structure of the radical common to all of them.
2. (a) Define the term *basicity of an acid*. (b) How do you account for the fact that acetic acid is monobasic, though each molecule of it contains four atoms of hydrogen?
3. Write the formula for each of the following salts: (a) lead acetate; (b) magnesium citrate; (c) calcium stearate.
4. (a) In what way do esters differ from salts in composition? (b) Give the general method for the preparation of each from a typical acid.
5. Give the chemical name and formula for each of the following compounds: (a) cream of tartar; (b) sugar of lead; (c) Rochelle salt; (d) nitroglycerin. (e) To what class of compounds does each of these compounds belong?
6. (a) How could you distinguish between cider vinegar and distilled vinegar? (b) Write the equations for the reactions that take place in the manufacture of each of these vinegars.
7. How does olive oil differ in composition from lubricating oil?
8. (a) How does butter differ in composition from oleomargarine? (b) Do you think it justifiable to allow the artificial coloring of butter without the payment of a tax, but not of oleomargarine?
9. What would be the result to one's health of eating foods that contain no (a) vitamin A; (b) vitamin B; (c) vitamin C; (d) vitamin D?
10. Distinguish between alcoholic fermentation and acetic fermentation.
11. The radical C_3H_5 is trivalent and is named glyceryl. Write the formula for the glyceryl ester of each of the following acids: (a) butyric; (b) palmitic; (c) stearic; (d) oleic.
12. Write the complete equations for the reactions that take place in each of the following: (a) ethyl alcohol + oxygen \longrightarrow ; (b) acetic acid + ethyl alcohol \longrightarrow ; (c) ethyl acetate + sodium hydroxide \longrightarrow ; (d) tartaric acid + potassium carbonate \longrightarrow ; (e) citric acid + magnesium carbonate \longrightarrow ; (f) stearin + sodium hydroxide \longrightarrow ; (g) sodium stearate + magnesium sulfate \longrightarrow ; (h) glycerin + nitric acid \longrightarrow ; (i) olein + hydrogen \longrightarrow .

Problems

1. One hundred grams of sucrose will yield how many grams (a) of alcohol when fermented? (b) of acetic acid?
2. (a) Calculate the weight of sodium hydroxide required to saponify 100 g of stearin. (b) What products would be formed? (c) Calculate the weight of each.

3. The Federal law requires that vinegar sold on the market must contain not less than 4 per cent by weight of acetic acid. A chemist found that 50 g of a certain sample of vinegar required 30 cc of a normal solution of sodium hydroxide to neutralize the acetic acid present. Does the vinegar meet the law's requirement?

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- The magazine *Fortune* contains the following articles, all well illustrated with colored pictures: "Plastics," Vol. XIII, No. 3, p. 69; "Diet," Vol. XIII, No. 5, p. 86; "Milk," Vol. XX, No. 5, p. 83; "Frozen Foods," Vol. XIX, No. 6, p. 61; "Nylon," Vol. XXII, No. 1, p. 57.
- Industrial and Engineering Chemistry*, Vol. XXXII, pp. 293-320, contains a number of articles on the general subject "Plastics and Resins from Hydrocarbons."
- The magazine *Life*, March 25, 1940, contains an interesting article on plastics, with colored illustrations.

CHAPTER 30

Metals and Their Compounds; Alloys

METALS																NONMETALS							
Li	Be																	B	C	N	O	F	He
Na	Mg																	Al	Si	P	S	Cl	A
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr						
Rb	Sr	Yt	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe						
Cs	Ba	R.E.	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	—	Rn						
—	Ra	Ac	Th	Pa	U																		

FIG. 312. Location of Metals and Nonmetals in Periodic Table

Introduction. In the previous chapters we have been studying the physical properties and chemical behavior of a considerable group of elements called the nonmetals. While differing greatly among themselves, they have the common property of forming acids. The elements yet to be described are as a group called *metals*, a few of which have been already described incidentally.

THE METALS

The metals. The word *metal* is an old and familiar one that at once brings a clear picture to the mind of every one of us. We think of iron and steel, of copper wire, of coins of silver or gold, of platinum jewelry, of aluminum saucepans. There are many more metals than nonmetals, and they differ among themselves greatly in many characteristics; consequently it is difficult to frame a simple yet accurate definition that covers the entire group.

We think of the metals as heavy bodies (high density), and most of them are; but a few, such as lithium or sodium, are lighter than water. With the notable exception of mercury, all metals are solids at ordinary temperatures, though cesium and gallium will melt on a hot summer day. Most metals are more or less *malleable* — that is, capable of being rolled or hammered into thin sheets; and *ductile*, or capable of being drawn into wire. Most metals are hard, some very hard; others, like sodium or lead, can be cut with a knife. Probably the most general characteristics of metals are (1) high conductivity for electricity and heat and (2) ability to reflect light

in a characteristic way from a polished surface, described as *metallic luster*. With the exception of copper and gold, this luster is silvery and not distinctive for any one metal.

Nature of the metallic state. The atoms of those elements that have metallic properties possess few valence electrons — usually less than 4. The vapors of the metals consist almost entirely of single atoms; and crystals of metals are made up of single electrically neutral atoms closely packed together in such a way that each atom is in contact with a number of similar atoms (usually 8 or 12, Fig. 313). The valence electrons are in some way divided up so that each atom has a partial valence connection with each of its neighbors.

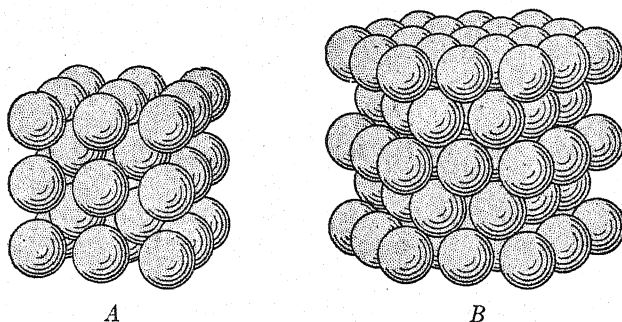


FIG. 313. *Typical Metallic Structures: (A) Body-Centered Cubic; (B) Close-Packed Hexagonal*

This arrangement is very different from the alternating positive and negative ions in a crystal of a salt, or that of neutral covalent molecules in a crystal of sugar or carbon dioxide held in place by attractive forces (van der Waals forces, p. 114). It is this peculiar relation of the valence electrons that gives the metals their *distinctive* property of high electrical conductivity. In some way the electrons distributed between the metallic atoms are free to move; and when they are directed by difference of potential at the ends of a wire, their motion constitutes metallic conduction. *All* the current is carried by the moving electrons, *none* by moving metallic atoms. This is in sharp contrast with conduction in a solution of an electrolyte, in which the current is carried by the movement of both cation and anion.

This same electron mobility within the crystals of a metal is doubtless responsible for the metallic luster common to all metals. It is also true that the arrangement of atoms within the crystals lends itself to ready deformation (malleability and ductility).

Properties of metals variable. The physical properties of metals are greatly modified by the presence of even small percentages of impurities, as well as by the mechanical treatment to which the metal has been subjected. A very little arsenic greatly modifies the electrical conductivity of copper; a few tenths of 1 per cent of carbon changes soft iron into steel. When cooled from the liquid state under proper conditions, a given weight of metal may be obtained as a continuous *single crystal*; but ordinarily it will freeze into an enormous number of separate *crystal grains* because crystallization will start at many points. The properties of the solid metal will depend on the size of these grains, on the heat treatment during cooling (annealing and quenching), and on the mechanical treatment (rolling and forging). Consequently in giving exact numerical values to some of the properties of the metals, it is necessary to state the conditions of treatment of the metal for which the properties are given.

Chemical characteristics of metals. The metals are *electropositive* in character; that is, metallic atoms tend to lose their valence electrons and become positive ions. The hydroxides of the metals are *bases*. In general, the hydroxides of metals of low valence are the strongest bases, while those of higher valences are weak or even amphoteric (p. 415) in character. Accordingly metals are sometimes defined as the base-forming elements. As we shall see, some of the metals can be oxidized to high valences (above 4) and so take on properties of nonmetals. They then tend to build up covalent negative ions with oxygen to form acids. Examples of such acids are chromic acid, H_2CrO_4 , and permanganic acid, HMnO_4 .

Since the metals readily part with their valence electrons, they are reducing agents of various strengths. They range all the way from the extremely active alkali metals (sodium, potassium) to the very inactive (noble) metals, such as gold or platinum.

Occurrence of the metals in nature. A few of the metals are often found in nature in the uncombined, or elementary, state, and are then said to occur *native*. Among these are gold, platinum, copper, bismuth, and in general all those that stand low in the electromotive series. As a rule, the metals are found in the form of oxides, sulfides, hydroxides, and salts of various acids. The most abundant of these salts are the silicates, carbonates, and sulfates. All such natural substances as are essentially chemical individuals, whether they contain a metal or not, are called *minerals*. Those natural products, whether minerals or mixtures of a number of minerals, which are of value for the extraction of useful substances,

are called *ores*. It sometimes happens that the ore-mineral occurs in lumps relatively free from secondary minerals, and it is then possible to hand-pick it in pure enough form to start at once upon its reduction. As a rule, however, the natural ore must undergo a process of concentration before the extraction of the metal can be undertaken.

Concentration. Most of the heavier metals, such as zinc, copper, lead, silver, and gold, are found either as sulfides or as native metals. The rich deposits of the world have become largely exhausted, and it is now necessary to use low-grade ores — often containing as little as 1 per cent of the desired metal. These ores must be crushed and the valuable portion *concentrated* before the metals can be obtained from them. The principal methods for concentrating the ores are the following:

1. **By washing.** This may be accomplished by stirring the crushed ore in running water. The worthless rock material is lighter in density than the metal mineral and is largely washed away, leaving the heavier ore in concentrated form.

2. **By flotation.** A second ingenious and effective method of concentration is called *flotation*. The finely crushed ore is churned up into a froth with water and a little oil — often pine oil or cresylic acid. Although the particles of sulfides or of metals are much heavier than either water or the powdered rock, when coated with oil they stick to the bubbles of froth, and are *float*ed off with the froth into settling-basins, from which a very concentrated ore is recovered for reduction (Fig. 314). Were it not for this flotation process, the heavy-metal industries would be in a bad way, for it would not pay to work most of our mines.

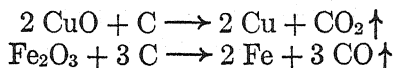
In general, the process is limited to those minerals that have a metallic luster — chiefly free metals or sulfide ores — and is most used with ores of copper, lead, and zinc. It is not, however, exclusively limited to such minerals. Coal can be so concentrated, and the process has been applied with marked success to the small particles of phosphate rock in Florida. Many millions of tons of ore of various metals are concentrated annually by flotation in the United States. In actual operation small quantities of various chemicals (about 1 oz to the ton) are added as may be needed to secure the best results.

3. **By the use of a magnetic field.** A number of minerals are more or less magnetic. Advantage may be taken of this property to separate a mixture of minerals.

Extraction of metals from ores; metallurgy. The process of extracting a metal from its ores is called its *metallurgy*, and in general it consists of two steps: *roasting* and *smelting*. Preliminary to smelting the ores are often heated with free access of air, or *roasted*. The purpose of this operation is to drive off water, carbon dioxide, or other volatile matter and to burn at least some of the sulfur of the sulfides into sulfur dioxide. *Smelting* is the winning of the metal from the prepared ore, and the details differ for each metal and for each type of its ores available. These details will be described more at length in connection with a few of the familiar metals. At this time it is desirable to emphasize merely the chemical principles that underlie the common types of metallurgy. In a very general way these are

1. **Reduction by electrolysis.** Metallic zinc may be deposited on the cathodes from a solution of zinc sulfate or other soluble zinc salt in water (p. 270); but to liberate sodium we must electrolyze a *molten* compound of the metal (its chloride or hydroxide, p. 282). Metals that act rapidly on water, such as sodium or magnesium, are obtained by electrolysis of fused salts. Some ores of copper or zinc are dissolved by acids, and the metal is obtained by electrolysis of such solutions.

2. **Reduction of an oxide by carbon.** Many of the metals occur in nature in the form of oxides or in minerals that can be converted into oxides. When these oxides are heated with carbon, they are nearly all reduced, as illustrated in the equations



The carbon is oxidized either to the dioxide or to the monoxide, according to the temperature which it is necessary to employ. High temperatures result in the formation of carbon monoxide.

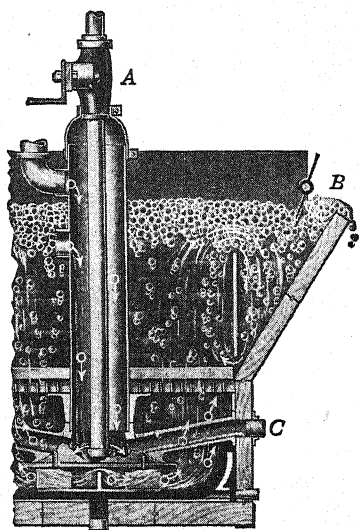


FIG. 314. *The Flotation Process*

Powdered ore, water, oil, and air are delivered into the shaft A and beaten to a froth by the fan at the base of the shaft. Air bubbles carrying the values in the ore rise as a froth and overflow at B. The worthless gangue sludges off at C

The chief difficulty with this method is that at very high temperatures many of the metals combine with excess of carbon to form *carbides*, so that the carbide rather than the free metal is obtained.

3. Reduction of an oxide or a sulfide by aluminum. When a very high temperature is required for carbon reduction, and the tendency of the metal to form a carbide is great, aluminum may sometimes be used as the reducing agent in place of carbon. For example, the element chromium may be prepared in this way :

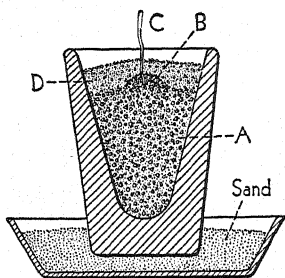
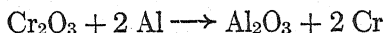
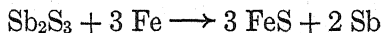


FIG. 315. Diagram Illustrating the Goldschmidt Method



This method is known as the Goldschmidt method, since it was developed by a German chemist of that name.

Just as oxygen may be removed from an oxide by aluminum, so sulfur may sometimes be removed from a sulfide by aluminum or by iron. For example, antimony and lead are sometimes desulfurized by scrap iron :



Preparation of chromium by the Goldschmidt method. A mixture of chromium oxide and aluminum powder is placed in a Hessian crucible (A, Fig. 315), and on top of it is placed a small heap B of a mixture of sodium peroxide and aluminum, into which is stuck a piece of magnesium ribbon C. Powdered fluorspar D is placed around the sodium peroxide, after which the crucible is set on a pan of sand and the magnesium ribbon is ignited. When the flame reaches the sodium peroxide mixture, combustion of the aluminum begins with almost explosive violence, so that great care must be taken in the experiment. The heat of this combustion starts the reaction in the chromium oxide mixture, and the oxide is reduced to metallic chromium, which collects in the bottom of the crucible.

ALLOYS OF THE METALS

Alloys of metals. A few of the metals, such as copper and aluminum, find large uses in very pure form. A vast amount of *nearly* pure iron is used ; but, as we shall see, it is necessary for most purposes to have certain other elements present in order that the iron may have the properties we usually want it to have. In the great majority of cases the metallic objects we use or see every day are made not of *one* metal but of two or more metals melted together and

called *alloys*. For example, gold jewelry, silver plate, coins of all kinds, brass, bronze, pewter, most objects of iron (such as automobile parts, Fig. 317), are alloys.

TYPICAL REACTIONS		REACTIVITY	METAL	EASE OF REDUCTION	BEHAVIOR TOWARD HYDROGEN	REDUCED FROM COMPOUNDS BY	OCCURRENCE IN NATURE
React with oxygen to form oxides	React with acids	Decreasing reactivity ↓	Li	Increasing ease of reduction ↓	Not reduced by hydrogen	Electrolysis of melted salt	Combined form only
			K				
			Ca				
			Na				
			Mg				
			Al				
			Mn				
			Zn				
			Cr				
			Fe				
	Cd						
	Co						
	Ni						
	Sn						
	Pb						
Oxides formed indirectly	React with steam	H	Reduced by hydrogen	Electrolysis of water solutions of salts or carbon reduction			
		Cu					
		Sb					
		Bi					
		As					
Oxides formed indirectly	React with cold water	Hg	Reduced by heat alone	Electrolysis or heat	Free and combined form		
		Ag					
		Pt					
		Au					
		Usually native metals					

FIG. 316. Summary of Relationship among the Metals

The nature of alloys. When two melted metals are mixed together, they act much like any other pair of liquids. (1) Some melted metals mix in all proportions, like sulfuric acid and water, and this is the case with lead and antimony. (2) Some may have a limited solu-

bility, each in the other (like ether and water). In this case the mixture separates into two layers, both saturated solutions, the lighter floating on the heavier. Lead and zinc are a pair of this kind. (3) Some may combine in various proportions to form definite compounds, more or less soluble in the excess liquid. (4) Some may be practically insoluble in each other, like oil and water. As the melt cools, the crystals that form may be pure metals, solid solutions of one metal in the other, compounds, or mixtures of any of these. Alloys therefore exhibit great variety both in nature and in structure.

Solid solutions. In some cases two melted metals mix in all proportions, and the crystals that separate on cooling contain the two metals in about the proportions in which they were present in the melt. Such crystals are called *solid solutions* because, though they closely resemble liquid solutions, they are solids.

Thus, when zinc and copper are melted together, as a rule in the proportion of about one atom of zinc to two or three of copper, and the solution is allowed to cool and crystallize, we obtain *brass*. X-ray analysis shows that brass of this composition crystallizes in a lattice like that of copper, but that the zinc atoms have replaced some of the copper atoms, generally at the corners of the cubes of the lattice. Therefore brass is not a mixture of tiny crystals of zinc and of copper, but is a far more fine-grained mixture of the actual atoms themselves. Zinc atoms are *dissolved* in the lattice of the copper atoms.

The eutectic. If we add a little antimony to melted lead and allow the solution to cool slowly, we find that crystals of *pure lead* separate and that the temperature at which crystal formation begins is below the melting point of pure lead. If we add a little lead to melted antimony and cool the solution, crystals of *pure antimony* form below the melting point of antimony. Each of these metals lowers the solidifying point of the other. The more of the solute metal we add, the lower is the temperature of crystal formation.

It is evident that if we melt the two metals together in every possible proportion, we shall obtain one particular mixture that will have a lower solidifying point than any other. At this lowest freezing point, crystals of *both* metals are deposited side by side. This mixture is called the *eutectic* of the two metals, and its melting point (or freezing point) is called the *eutectic temperature*. At this temperature the proportion of the two metals in the melt and in the mass of depositing crystals is the same and is constant for a given pair of metals. In physical structure the eutectic is a fine-grained conglomerate of crystals of the two metals.

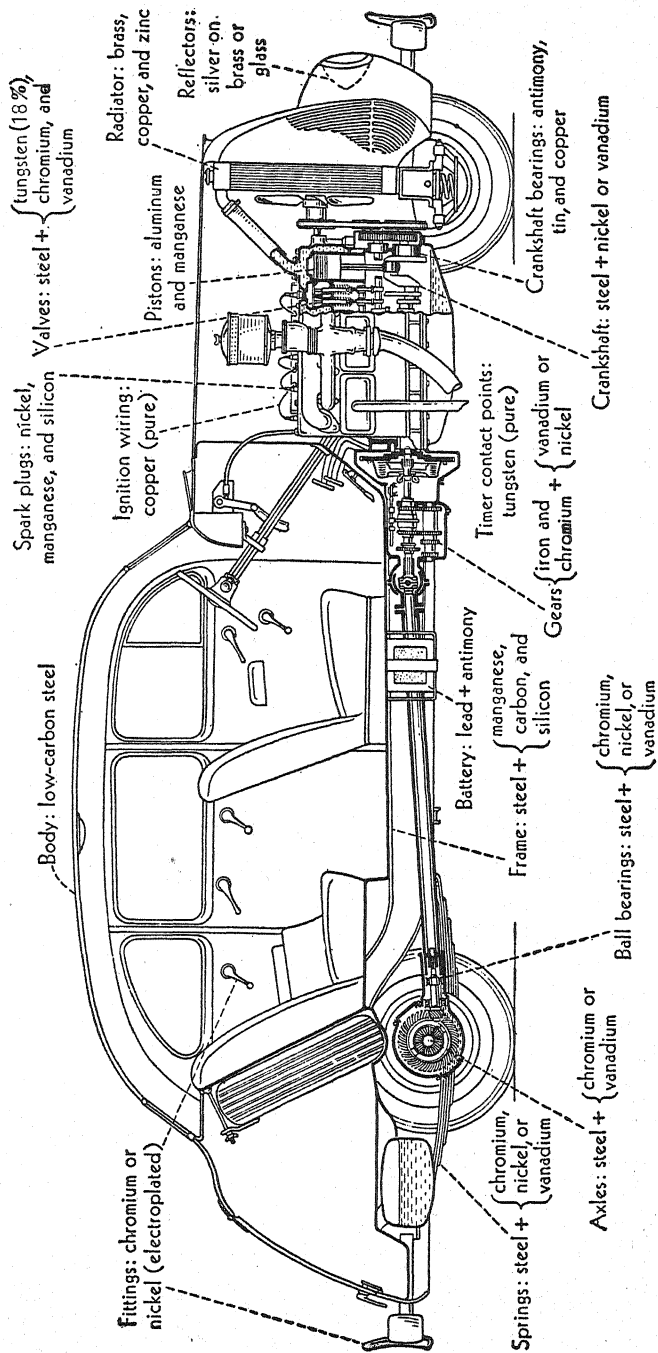


FIG. 317. Diagram Showing Some of the Alloys Used in the Construction of an Automobile

While it is usually true that each metal *lowers* the melting point of the other, it sometimes happens that the melting point of one metal or even of both metals is *raised* by the addition of the other. Thus, alloys of sodium with mercury are solids at ordinary temperatures, though mercury melts at about -40° . Sometimes a eutectic is formed between two compounds or between two solid solutions.

Eutectic diagram. In the diagram (Fig. 318) let us indicate the composition of the alloy along the line AB divided into 100 divisions. Let $A = 100$ per cent antimony and $B = 100$ per cent lead. C , which is halfway between A and B , will then represent 50 per cent each of antimony and of lead, and E'' 80 per cent lead and 20 per cent antimony.

The vertical lines AT and BT represent temperature, A' being the melting point of antimony and B' that of lead. If to pure lead we add a small percentage of antimony, the freezing point is lowered, the fall with increasing quantities of antimony being shown by the sloping line $B'E$. Similarly, if to pure antimony we add increasing quantities of lead, the fall in freezing point is shown on the sloping line $A'E$. The point E is thus the lowest temperature at which any mixture of antimony and lead can remain liquid, and is therefore the *eutectic temperature*. The composition of the liquid at this point (E'') is called the *eutectic composition*.

Triple and quadruple alloys. We may melt together three metals to form a triple alloy, or four to form a quadruple alloy. To meet certain industrial requirements an even larger number of metals may be used. Just as two metals have a definite eutectic temperature and composition, so we may have a triple or quadruple eutectic, each with its definite eutectic temperature and composition. Many commercial alloys are approximate eutectics, for eutectics have a dependable, fine-grained structure that other alloys are apt to lack.

Freezing point of alloys. Apart from a eutectic mixture an alloy cannot be said to have a true melting (or freezing) point. Some melted mixtures *begin* to deposit a solid solution at a given temperature; but as solidification proceeds, the composition of the solid changes, as does also the freezing point, so that the freezing extends over a definite range of temperature. If the freezing results in a eutectic, then the melt *begins* to solidify at a given temperature, which depends upon the metals present and their proportions. As the temperature falls, the freezing progresses; and only at the eutectic temperature is freezing complete. A *eutectic* mixture melts and freezes at a perfectly definite temperature, like a pure metal.

Structure of alloys. When we cool a melted mixture of metals, one or the other pure metal or a compound or a solid solution at first

separates. As the temperature falls, the crystals of these solids grow in size and in number, the composition of the remaining liquid changing as a result, until finally the eutectic temperature is reached and the liquid has the eutectic composition. At this temperature the entire remaining liquid slowly solidifies as a mass of very small, intimately mixed crystals of the various components present.

It will be seen that if no precautions are taken, the solid alloy is likely to consist of rather large crystals of some kind embedded in a fine cement of small eutectic crystals. Such a structure is unsuited to many technical uses. Rapid cooling tends to keep all crystals small and well mixed; and the nearer the composition of the alloy approximates a eutectic, the more homogeneous will be the structure. Some solid solutions are relatively free from the tendency to form large crystals, and are homogeneous in structure.

Properties of alloys. In general, the properties of an alloy of two metals cannot be predicted with any certainty from those of its constituent metals, though some properties, such as density, are apt to be a rough average of those of the constituent metals. It seems entirely reasonable that the color of brass should be golden, since it is composed of reddish copper and silvery zinc; but silvery nickel almost completely overcomes the color of copper, as is evident in our five-cent coins, and both silver and cadmium give gold a greenish tint, though they are silvery in color.

As we have seen, the freezing point of an alloy composed of two metals is usually below that of either component if they form a simple eutectic; but if they form solid solutions, the temperature at which solidification is complete may be at some intermediate point. As a rule, an alloy is harder than either component, and the electrical conductivity is less. For this reason most kinds of resistance wires are alloys. Many alloys (for example, stainless steel) resist chemical corrosion better than their components taken separately, so that alloys find increasing use in chemical industries.

If the alloy is triple or quadruple, or if a nonmetal such as boron, silicon, or phosphorus is one of the components, the properties of the alloy become even less predictable.

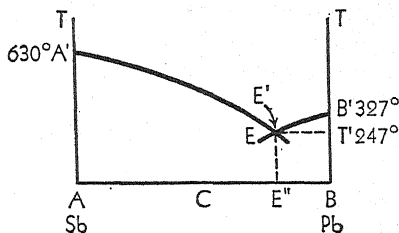


FIG. 318. *Diagram Illustrating the Eutectic of Antimony and Lead*

Future of alloys. A considerable number of alloys have been in common use for a very long time. Among these are brass, bronze, pewter, solder, type metal, and coinage metals. Some of these long ago became more or less standardized in composition because their uses formerly were rather definite. The period of diversified machinery, especially electrical devices, does not date back much beyond half a century, and the call for metal materials to meet an ever-increasing variety of purposes is very insistent, so that the production of new alloys adapted to exactly specified purposes has become one of the most important problems for the metallurgist and chemist. Some large firms do nothing but manufacture alloys guaranteed to have almost any specified properties — they make metal bodies to order.

It should be remembered that there are many metals which as yet have found no important uses in pure condition and whose alloys have been little studied, that almost any number of metals and even some nonmetals can be combined in an alloy, and that the relative proportions of each can be varied within wide limits. It will then be seen that the field of alloys is a rich and fascinating one for the scientist as well as for the inventor.

Alloys of antimony and bismuth. By way of illustration it will be well to describe briefly some of the alloys of antimony and bismuth — two semimetals described in Chapter 22. Other alloys will be referred to in succeeding pages in connection with the various metals.

Antimony and bismuth are both very heavy, low-melting metals, and some of their alloys melt at a still lower temperature. Antimony has the somewhat unusual property of expanding in the act of

Table of Some Common Alloys Containing Antimony or Bismuth

NAME	LEAD (Per Cent)	TIN (Per Cent)	ANTIMONY (Per Cent)	BISMUTH (Per Cent)	COPPER (Per Cent)
Type metal	70	10	18		2
Britannia metal		91-85	9-11		0.2-1 (Zn0-3)
Pewter	0-20	89-74	0-7.6		0-3.5
Babbitt metal (genuine) .		89	7.3		3.7
White metal* (tin base) .	12-40	74-42	9.5-16		1-4.2
White metal* (zinc base)	Zn 88	2	2		8
Rose's metal (m.p. 93.8°)	28	22		50	
Wood's metal (m.p. 60.5°)	25	12.5		50	Cd 12.5
Newton's metal (m.p. 94.5°)	31	19		50	

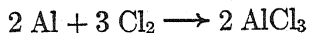
* *White metal* is a general term for a large group of alloys, of which those listed in the table above are examples.

solidification, and many of its alloys share this property. This is an important property in making type; for the cast type in expanding fits the mold tightly, and the fine lines are emphasized in the cast and not obliterated, as would occur if contraction took place. Many of these alloys are fairly hard and take a smooth polish. They are much used for bearings in machinery. Bismuth is a component in a number of very low-melting alloys which are used as safety links or plugs in fire curtains, boilers, and fuses.

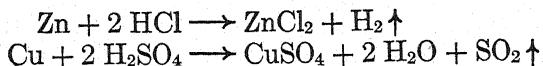
COMPOUNDS OF THE METALS

Preparation of compounds of the metals. A great many methods are employed in the preparation of compounds of the metals. These compounds, which include oxides, hydroxides, and salts, are very numerous, and each has its own peculiarities which must be taken into account in devising means for preparing it. In many cases some rather unusual method is employed, owing to the character of the minerals available in nature or to the accumulation of a cheap by-product in some industry. Naturally the methods employed on a small scale in the laboratory are likely to differ from those used in the industries, where economy is the first requirement. There are, however, some general principles which underlie the great majority of these methods, a clear understanding of which will save time and effort in remembering the details in a given case.

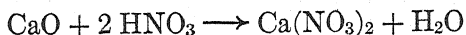
1. *Direct union of two elements.* Very many binary compounds may be prepared by heating the metal with the appropriate non-metal. Among these are oxides, sulfides, and halides. The product in such cases is, of course, anhydrous, and this method finds wide application when it is the *anhydrous* rather than the *hydrated* compound that is wanted. The method is most frequently employed in the preparation of anhydrous halides, as, for example, aluminum chloride:



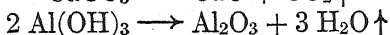
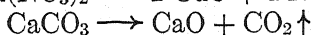
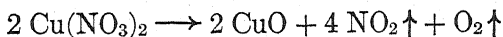
2. *Treatment of a metal or its oxide, hydroxide, or carbonate with an acid.* Many of the metals are produced commercially in a high degree of purity and at small cost, and these are often the most convenient starting point for the preparation of their compounds on a laboratory scale. For example, the salts of zinc and copper are frequently made in this way:



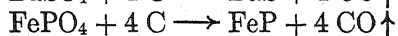
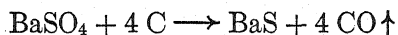
In the industries the hydroxide, oxide, or carbonate is more likely to be employed, since it is usually found in nature or is easy of preparation. For example, calcium salts are often prepared from lime (CaO), as in the case of the nitrate:



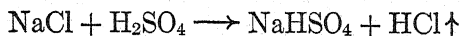
3. Decomposition of a compound. The decomposition of a compound, either by heat alone or aided by a reducing agent, frequently leads to the formation of simpler ones. For example, nitrates, carbonates, and hydroxides, when heated sufficiently, usually yield oxides:



When heated with carbon the various salts of oxygen acids are usually reduced and yield a binary compound of the metal with the acid-forming element. For example, sulfates yield sulfides, and phosphates yield phosphides, as shown in the equations



4. Displacement of a volatile acid. When a nonvolatile acid acts upon a salt of a volatile acid, the latter is displaced in accordance with the general principles of equilibrium, *provided the volatile acid is sparingly soluble in any liquid that may be present*. For example, the reaction of sulfuric acid with sodium chloride goes on to conclusion if the sulfuric acid employed is quite concentrated, for hydrogen chloride is very sparingly soluble in this liquid:

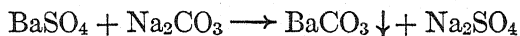


In dilute solution the reaction results in an equilibrium, for in this case the hydrogen chloride is freely soluble in the solution.

5. Methods based upon precipitation. The formation of a precipitate when two electrolytes are brought together in solution takes place in accordance with the principles of ionic equilibrium developed in Chapter 19. *In general, it may be said that when two salts, or a strong acid and a salt, are brought together in solution, double decomposition takes place with the formation of a precipitate if the union of any pair of ions produces an insoluble salt.* When a salt of a strong acid is treated with a weak acid, however, no precipitate is formed, even though double decomposition would result in the formation of

an insoluble salt, unless the latter is extremely insoluble. It can also be shown that the *salts of strong acids*, such as sulfates or chlorides, when insoluble in water *are also insoluble in dilute acids*. *Salts of weak acids*, such as carbonates, sulfites, and sulfides, though insoluble in water, *are soluble in dilute acids*. These principles are of constant application in the preparation of compounds.

6. Fusion reactions. When compounds are melted together, it sometimes happens that double decomposition occurs, which would not take place if the same salts were brought together in water. In such fusion reactions one of the melted salts may be regarded as the solvent, and it is to be expected that the solubility of the other in this solvent will be different from its solubility in water. For example, barium sulfate is practically insoluble in water, and consequently it is not greatly affected by aqueous solutions of sodium carbonate. *In melted sodium carbonate*, on the contrary, it is readily soluble, while barium carbonate is insoluble. As a consequence, when it is melted together with sodium carbonate, the following double decomposition takes place:



When the mixture is cooled and then digested with warm water, the sodium sulfate dissolves, leaving the barium carbonate, which may then be filtered off and converted into any desired salt. This forms a convenient method of passing from an insoluble salt of a strong acid to a similar salt of a weak acid. It will be recalled that natural silicates can be decomposed in the same way.

Insoluble compounds. It is evident that a knowledge of the solubility of compounds is an important part of a training in chemistry. With this knowledge it is possible, in many cases, to predict the course of a reaction and to devise ways in which to prepare desired compounds. For precise information a dictionary of solubilities must be consulted, but it is possible to make a few general statements, which will be of assistance in understanding the reactions described in the following chapters. These statements apply only to normal salts of the more familiar elements. Acid salts are likely to be more soluble than normal salts, and basic salts less so.

1. **Hydroxides.** All hydroxides are insoluble in water except those of ammonium, sodium, potassium, calcium, strontium, and barium.

2. **Nitrates.** All nitrates are soluble in water.

3. **Chlorides.** All chlorides are soluble in water except silver and mercurous chlorides. (Lead chloride is but slightly soluble.)

4. **Sulfates.** All sulfates are soluble in water except those of barium, strontium, and lead. (Sulfates of silver and calcium are only moderately soluble.)

5. **Sulfides.** All sulfides are insoluble in water except those of ammonium, sodium, and potassium. The sulfides of calcium, strontium, barium, and magnesium are insoluble in water but are changed by hydrolysis into acid sulfides which are soluble. On this account they cannot be prepared by precipitation.

6. **Carbonates, sulfites, phosphates, and silicates.** All of these normal salts are insoluble in water except those of ammonium, sodium, and potassium. Magnesium carbonate is slightly soluble.

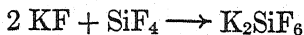
For further information concerning the solubilities of compounds of the metals, consult table in Appendix.

DOUBLE AND COMPLEX SALTS

In the preceding pages a number of compounds have been represented by formulas which indicate that they are made up of a combination of two different salts. The formula of cryolite is often written $\text{AlF}_3 \cdot 3 \text{NaF}$; the fluosilicates were formerly given such formulas as $\text{SiF}_4 \cdot 2 \text{KF}$; and alum, often written $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24 \text{H}_2\text{O}$, is another example of the same general character. Among these salts two extreme cases can be defined.

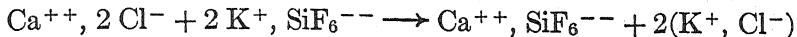
1. **Double salts.** Carnallite ($\text{KCl} \cdot \text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$), a well-defined crystalline compound, is a good example of a *double salt*. When it is dissolved in water, the solution acts as though it contained a mixture of the chlorides of potassium and magnesium, both of which are freely ionized. Silver nitrate precipitates all the chlorine as silver chloride; ammonium phosphate precipitates the magnesium as magnesium ammonium phosphate (MgNH_4PO_4). *A salt of this kind, which in solution decomposes into its constituent salts and gives reactions for their individual ions, is called a double salt.*

2. **Complex salts.** Potassium fluosilicate (K_2SiF_6) may be taken as an example of a *complex salt*. It can be prepared by bringing together in solution the fluorides of potassium and silicon:



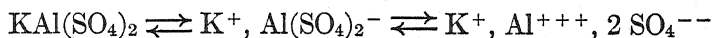
The product of the reaction cannot properly be regarded as a double salt, for it gives none of the reactions characteristic of the fluorides from which it is formed. Thus, when calcium chloride is treated with potassium fluoride, calcium fluoride precipitates. With fluo-

silicates, on the other hand, calcium chloride enters into double decomposition, as shown in the equation



The complex ion SiF_6^{--} takes part in all the reactions of the fluosilicates. This fact, together with the stability of the salts, has led chemists to regard the fluosilicates as salts of fluosilicic acid (H_2SiF_6) rather than as made up of two different fluorides, as in the case of double salts. *Compounds of this kind, which yield ions other than those of the salts from which they may be formed, are called complex salts.*

Intermediate types. The two classes just described are extremes. There is every gradation between them, and alum, whose formula may be written $\text{KAl}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$, is an example of an intermediate type. In rather concentrated solution some alum molecules dissociate into the constituent sulfates, which then give their individual ions; and some act as a complex, giving the alkali metal as one ion and the remainder of the alum as the other. These transitions constitute an equilibrium which may be represented thus:



As the solution is diluted more and more, the complex ion $\text{Al}(\text{SO}_4)_2^{-}$ tends to dissociate more completely into its constituent ions, which are those of a simple salt.

Questions

1. (a) What is the difference between a mineral and an ore? (b) Is crude petroleum an ore? (c) Is rock salt a mineral? (d) Is it an ore?
2. It is a difficult matter to prepare any one metal in a perfectly pure state. What reasons can you give for this?
3. Detail the general physical characteristics of the metals, and contrast the chemical conduct of the metals and the nonmetals.
4. What is the meaning of the following terms: (a) *metallurgy*; (b) *malleable*; (c) *single crystal*; (d) *crystal grain*; (e) *flotation*; (f) *eutectic*; (g) *electrolysis*?
5. (a) What cases can you cite of compounds formed between two nonmetals? (b) Are intermetallic compounds ever formed in an alloy?
6. Why should alloys be superior to pure metals for many purposes?
7. Suggest a method for preparing each of the following compounds: (a) ferrous sulfate (FeSO_4); (b) silver sulfide (Ag_2S); (c) silver bromide (AgBr); (d) copper chloride (CuCl_2).

8. (a) Lead chloride is insoluble in acid solutions. What inference can you draw as to the strength of hydrochloric acid? (b) Heated with concentrated sulfuric acid, the products are lead sulfate and hydrogen chloride. How do you explain this?

9. Ferrous oxalate (FeC_2O_4) is insoluble in water. (a) When ferrous chloride (FeCl_2) and oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$) are brought together in solution, only a part of the iron is precipitated as oxalate. Why? (b) The addition of ammonium hydroxide causes complete precipitation. Why?

10. Distinguish between double salts and complex salts and give two examples of each.

Problems

1. One liter of water dissolves 8.35 g of silver sulfate at 25° . (a) Express this solubility in terms of gram-molecular weights per liter. (b) Assuming complete ionization, express the concentration of each ion in terms of gram-ionic weights per liter.

2. (a) In what three ways could you prepare 100 g of CuCl_2 ? (b) What weight of the copper-containing material will be required in each case?

3. One hundred grams of calcium carbonate (CaCO_3) is decomposed by heat. (a) What are the resulting products? (b) Calculate the weight of each.

4. What weight of copper sulfate (CuSO_4) can be prepared from 1000 g of copper?

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Electrochemistry

Introduction. We have seen that many chemical reactions involve readjustments of the electrons in the valence shells of at least some of the atoms concerned, while others involve a re-pairing of charged ions. All reactions are therefore electrical in character. Consequently it is not surprising to find that the movement of electrons during a chemical change may, under proper conditions, give rise to an electric current; and conversely an electric current (which is a movement of electrons) may bring about chemical changes. The science of *electrochemistry* is concerned with both these closely related types of changes.

Faraday's laws. We have already learned that when a current of electricity is passed through water containing a little sulfuric acid in solution, a chemical change takes place at each electrode; hydrogen is liberated at the cathode (— electrode) and oxygen at the anode (+ electrode). Over a hundred years ago the English scientist Faraday (Fig. 184) studied these changes and discovered some very significant facts, now generalized in what are called Faraday's two laws. These laws are fundamental to the science of electrochemistry.

Faraday observed that the weight of hydrogen or oxygen or silver or other element liberated at an electrode depends *solely* on the *quantity of electricity* that flows through the solution undergoing electrolysis. It does not depend at all on the temperature or the concentration of the solution, or the rate at which the charge flows, but only on the *quantity of electricity*. This fact constitutes Faraday's first law: *The amount of electrochemical change is directly proportional to the quantity of electricity that flows* (Fig. 319).

Faraday's second law has to do with the relation between the relative weights of the *different elements* liberated at the electrodes by the *same* quantity of electricity, and the gram-equivalent weights of those elements. The *gram-equivalent weight* of an element is its gram-atomic weight divided by its valence (p. 106). Faraday's experiments proved that if a given quantity of electricity is allowed to flow successively through a number of different solutions in series, the results may be summed up as Faraday's second law: *The weights of the various elements liberated at the electrodes are in the ratio of their gram-equivalent weights* (Fig. 319).

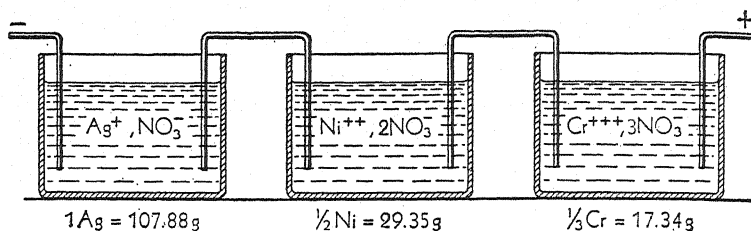


FIG. 319. Illustration of Faraday's Laws

To deposit the metallic atoms Ag, Ni, Cr from the solutions of the salts in which they occur as the ions Ag^+ , Ni^{++} , Cr^{+++} , each Ag^+ ion must recover 1 electron, each Ni^{++} ion 2 electrons, and each Cr^{+++} ion 3 electrons. One faraday of electricity furnishes enough electrons to silver ions to deposit 1 g-at. wt (1 g-equiv wt) of silver, but it can provide electrons for only $\frac{1}{2}$ g-at. wt of nickel (1 g-equiv wt) and only $\frac{1}{3}$ g-at. wt of chromium (1 g-equiv wt). A given current will deposit these three metals from solution in the ratio of their gram-equivalent weights (107.88 g Ag; 29.35 g Ni; 17.34 g Cr), whether the quantity of current passing consists of 100 electrons or of 100 billion

The quantity of electricity that will liberate exactly 1 g-equiv of an element is called a *faraday*; and it follows directly from the second law that 1 faraday will liberate 1 g-equiv of every element that can take part in electrochemical changes.

Ohm's law. This law applies to the flow of electricity through an electrolyte as well as through a wire or other metallic conductor, and it may be stated as follows: *The magnitude of an electric current flowing in a circuit is directly proportional to the electrical pressure (electromotive force) and inversely proportional to the resistance.* The relation between the current (i), the electromotive force (e), and the resistance (r) is shown by the following equation:

$$i = k \frac{e}{r},$$

in which k is a constant depending upon the units employed for the other factors.

Electrical units. The unit of resistance (r), called the *ohm*, is arbitrarily defined as the resistance at 0° of a column of mercury 1 mm² in cross section and 106.3 cm in length. The unit of quantity (i) is the *coulomb*; this is the quantity of electricity required to liberate exactly 0.001118 g of silver. The *ampere* (amp) is the unit of current and is defined as the flow of current equal to 1 coulomb/sec. When the electromotive force (e) is of such a value that it can drive a current of 1 amp through a resistance of 1 ohm, it is said to have the unit value of 1 volt (v). It is of interest to note that each of these electrical units bears the name of some great investigator in the field of electricity.

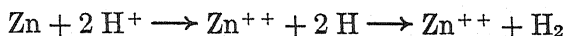
As a result of these definitions of *units* the k in the equation above becomes equal to 1, and the equation for Ohm's law may be written in the more usual form,

$$i = \frac{e}{r}$$

It is easy to calculate the number of coulombs in 1 faraday, thus: 107.88 (gram-equivalent of silver) $\div 0.001118 = 96,490$ coulombs.

Galvanic cells. Since an electric current, in passing through a solution, produces a chemical change, it is only natural to wonder whether the electrochemical effect can be reversed. Can we allow the chemical reaction to take place in such a way as to generate an electric current? The answer is yes. Such an arrangement, by which a chemical reaction produces electrical energy, is called a *galvanic cell*, or a *battery*. Many types of these cells have been developed, but we shall describe only a few.

Acid cell. If a zinc rod is dipped into a dilute sulfuric acid solution (Fig. 320, A), hydrogen is liberated and escapes in bubbles at the surface of contact between the zinc and the solution. The chemical change, expressed in terms of ions, is



Each zinc atom involved in the reaction loses 2 electrons to 2 hydrogen atoms. The resulting zinc ions go into solution and take the place of the hydrogen ions which come out of solution as hydrogen atoms; these atoms then double up to form molecules of hydrogen and bubble off as gas. It is an important fact that in this reaction a very considerable amount of heat is generated.

Now let us introduce a graphite rod into the solution along with the zinc (Fig. 320, B), not allowing the two rods to touch. The graphite rod has no effect, hydrogen continues to escape from the

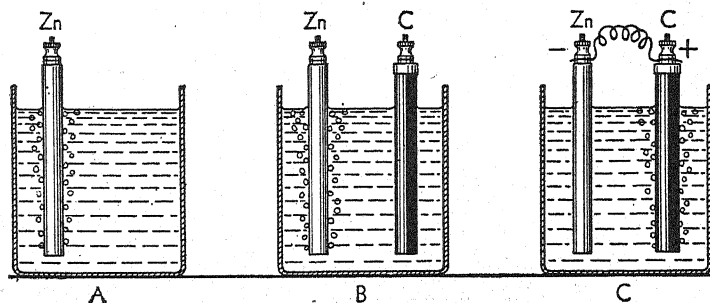


FIG. 320. Diagrams of Details of an Acid Cell

zinc, and heat is still generated. But if we now join the zinc rod to the graphite rod with a metallic conductor (say, a copper wire) in an external circuit (Fig. 320, *C*), two profound changes in the whole process take place: (1) While the zinc continues to dissolve, *the hydrogen now bubbles off from the graphite rod.* (2) *The heat generated is much less than before*; and with the use of a suitable electrical measuring instrument, we find that *an electric current is flowing* through the wire from one rod to the other.

Interpretation of the changes taking place in an acid cell. Our interpretation of these changes is as follows: The zinc atoms continue to dissolve as zinc ions; but their electrons, instead of being handed over directly to the hydrogen ions, push their way from the negatively charged zinc rod by way of the external circuit and onto the surface of the carbon rod, where the hydrogen ions in the solution find it easier to pick off the electrons (and become hydrogen atoms) than at the zinc surface. Exactly the same chemical reaction occurs as before. However, the energy liberated in the chemical reaction, which previously appeared entirely as heat, is now transformed in part into the electrical energy of the moving electrons, and the decrease in the amount of heat energy is exactly equivalent to the electrical energy generated.

The zinc rod is the negative pole of the cell, the carbon rod the positive pole; and the electric current (the stream of electrons) flows from the negative pole through the wire to the positive pole. However, it is still common practice to speak of the current as flowing from the positive pole to the negative, because of the survival of an old convention adopted long before much was known about the nature of electricity.

Polarization. The acid cell just described is not very efficient. It

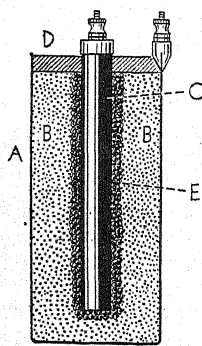
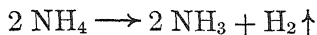


FIG. 321. Vertical Section of a Dry Cell

will function well for a brief time, but soon the hydrogen gas liberated at the graphite electrode forms a film on it that effectively insulates the graphite from the solution and builds up such a high resistance that the current virtually ceases to flow. An electrode in this condition is said to be *polarized*. It is evident that an effective cell must include some scheme for *depolarizing* such an electrode.

The dry cell. The widely used *dry cell* acts in essentially the same manner as the acid cell. A zinc vessel *A* (Fig. 321) contains moist ammonium chloride *B*, together with a carbon rod *C*. When con-

nection is made between the zinc and the carbon rod, zinc dissolves as zinc ions, and the resulting electrons flow through the external circuit to the carbon rod. Ammonium ions (NH_4^+) move to the carbon anode and regain their electrons at the carbon surface. Two neutral ammonium radicals then react with each other to form ammonia (which dissolves in the moisture) and hydrogen gas, thus:



A layer of manganese dioxide *E* is partially effective in *depolarizing* the carbon electrode by oxidizing the hydrogen which would otherwise collect as a film on the electrode. Millions of these dry cells are annually used for operating devices that require small currents for but brief time intervals, such as doorbells, flashlights, and telephones.

The Daniell cell. One form of the Daniell cell is shown in Fig. 322. The electrode *B*, made of thin sheet copper, is placed in the bottom of a jar and the jar nearly filled with a saturated solution of copper sulfate. A solution of zinc sulfate is floated on the heavier copper sulfate solution, and in this is immersed the zinc electrode *A*. When the two electrodes are connected by a wire, the electric current (stream of electrons) flows from the zinc through the wire to the copper.

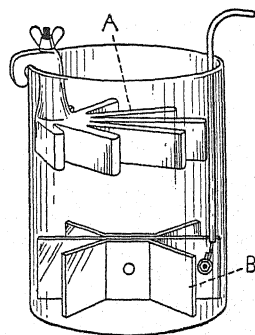


FIG. 322. A Simple Type of Electric Cell, Called the Daniell Cell

In the days before the electric dynamo came into wide use the Daniell cell (or crowfoot cell, as it was called) was one of the chief sources of electric current, and many thousands of miles of telegraph lines were operated by these cells. The cell is cited here, not because of its present-day importance, but because it affords a basis for discussing the mechanism of the electrochemical process that occurs at electrode surfaces.

Interpretation of the changes that take place in the Daniell cell. While we have no entirely satisfactory theory to account for the changes that take place in the Daniell cell, we may venture to give some of the details of one of the most generally accepted theories. In doing so we must be careful to distinguish between what is fact and what is theory.

Equilibrium between zinc and zinc ions. Let us again take a zinc rod *A* (Fig. 323); but instead of dipping it into an acid solution (as in the acid cell), let us dip it into a solution of *its own ions* —

for example, into a solution of zinc sulfate contained in the beaker B. With the proper instrument the zinc rod will be found to have a

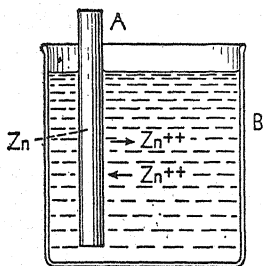


FIG. 323. *Equilibrium between Zinc and Zinc Ions*

negative charge — that is, an excess of electrons. According to the theory, the zinc surface atoms have a strong tendency (sometimes called *solution pressure*) to leave their valence electrons on the rod and pass into solution as ions, Zn^{++} ; and the zinc ions, already present in the solution, show a tendency (sometimes referred to as *osmotic pressure*) to deposit on the zinc rod.

In this way there results an equilibrium between the force driving the ions back on the rod to become atoms, and the force driving the atoms into solution as ions. In a given case this equilibrium will depend on the metal in question, the temperature, and the concentration of the ions in the solution.

Electromotive force. When equilibrium has been reached, in the case of zinc, there is an excess of electrons on the rod. The electrons repel each other; and if the rod were connected by a wire to some other suitable electrode, they would flow along the wire as an electric current that could be measured in volts. The intensity of this escape tendency is called the potential of the single electrode measured in volts. In general, the higher a metal stands in the electromotive series (p. 277), the greater is the negative potential of the electrode of the metal in a solution containing its ions at normal concentration.

For metals below hydrogen in the electromotive series, such as copper or silver, the case is different. If we use a copper electrode in a solution containing copper ions, there is little tendency for the copper atoms to become copper ions. On the contrary, there is a strong tendency for the copper ions to deposit on the surface of the copper electrode. Accordingly the copper electrode shows a positive charge, — that is, a deficiency of electrons, — and its potential is opposite to that of the zinc electrode. Therefore it is given a positive sign.

Single-electrode potentials. In the adjoining table are given a list of what are called single-electrode potentials. They represent the potential we may expect from an electrode of the metal dipped into a normal solution of its ions at 25° . These single potentials are very hard to measure with accuracy independently. Therefore they are expressed in terms of a hydrogen electrode in equilibrium with hydrogen ions, which is assumed to have zero potential. We can

now give definite values to the elements in the electromotive series, some of which are indicated in the table.

The zinc-copper cell. Suppose we should have a zinc rod *A* (Fig. 324) dipping into a solution of zinc sulfate, and a copper rod *B* dipping into a

Single-Electrode Potentials

ELECTRODE	POTENTIAL ₁ (VOLTS)
$\text{Mg} \rightleftharpoons \text{Mg}^{++}$	- 2.40
$\text{Zn} \rightleftharpoons \text{Zn}^{++}$	- 0.758
$\text{Fe} \rightleftharpoons \text{Fe}^{++}$	- 0.44
$\text{Cd} \rightleftharpoons \text{Cd}^{++}$	- 0.397
$\text{Ni} \rightleftharpoons \text{Ni}^{++}$	- 0.22
$\text{Pb} \rightleftharpoons \text{Pb}^{++}$	- 0.12
$\text{H}_2 \rightleftharpoons 2 \text{H}^+$	0.000
$\text{Cu} \rightleftharpoons \text{Cu}^{++}$	0.344
$\text{Ag} \rightleftharpoons \text{Ag}^+$	0.799
$\text{Hg} \rightleftharpoons \text{Hg}^{++}$	0.86
$2 \text{I}^- \rightleftharpoons \text{I}_2$	0.535
$2 \text{Br}^- \rightleftharpoons \text{Br}_2$	1.065
$2 \text{Cl}^- \rightleftharpoons \text{Cl}_2$	1.359
$2 \text{F}^- \rightleftharpoons \text{F}_2$	2.8

solution of copper sulfate, with the two solutions separated by a porous partition *D* to prevent mechanical mixing. On connecting the two electrodes by a wire, we should naturally expect a current to flow along the wire. The electrons which accumulate in the zinc rod repel one another and are thus pushed out along the wire. They are also pulled, or sucked, along the wire by the copper ions on the copper electrode. The single-electrode potential (push potential) of zinc dipping into a normal solution of its ions is about 0.76 v, and the single-electrode potential (pull potential) of copper in a normal copper ion solution is about

0.34 v. The driving force, or electromotive force, of the current ought to be the sum of the push and pull potentials, — namely, about 1.10 v, — and measurements show this to be the fact.

The cell in action. As the electrons leave the zinc to flow along the wire, the zinc ions in the solution, formerly held close to the surface of the zinc, are now free to move away, and more zinc surface atoms form new ions and maintain the supply of electrons on the zinc electrode. The electrons that are continuously reaching the copper electrode through the wire keep restoring electrons to the copper ions which hover around the copper-electrode surface. The resulting copper atoms separate on the copper-electrode surface. In the meantime the sulfate ions, deserted by the copper ions, move from the right-hand compartment through the porous partition and pair off with the zinc ions, dissolving off the surface of the zinc electrode. Thus the cell functions continuously, furnishing a steady current of constant electromotive force, without polarization of the electrodes.

Other cells. It is possible to construct different cells of the type of the Daniell cell, of various electromotive forces, by selecting suitable pairs of metals from the electromotive series. The *voltage* of the current depends not

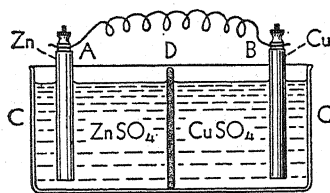


FIG. 324. A Zinc-Copper Cell

on the size, shape, or distance separating the electrodes, but only on the substances used in the electrodes and in the solutions. The *strength* of the current depends not only on the voltage but also on the external resistance and on the internal resistance of the cell, the latter, in turn, depending on the areas of the two metal plates.

Storage batteries. The cells, or batteries, that we have been considering (*galvanic cells*) turn chemical energy into electrical energy, but as a rule they are not reversible. In other cells, such as those used in the production of sodium (p. 282), the electric current is used to bring about reactions at the electrodes, and electrical energy is stored as chemical energy in the products of the electrolysis. Such cells are called *electrolytic cells*.

Sometimes a distinction is made between a cell and a battery. A cell consists of an electrolyte and a single pair of electrodes, while a battery consists of a group of cells, or an electrolyte with a number of anodes and cathodes. Usually it is not necessary to make the distinction.

Storage batteries, such as the lead cell or the Edison cell, are reversible arrangements that combine both types of cells. On being charged with a current they act as electrolytic cells, and the electrical energy given them is stored as chemical energy in the products of electrolysis deposited on the electrodes. While delivering current they act as galvanic cells, and the chemical energy of the electrode materials is converted into electrical energy.

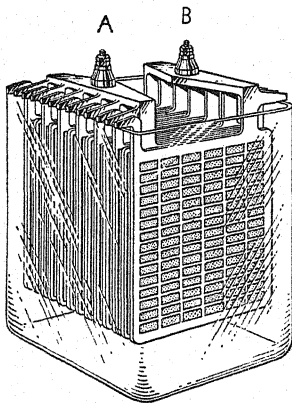
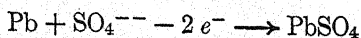


FIG. 325. A Seven-Plate Storage Battery

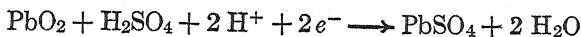
The lead cell. The lead cell, or ordinary storage battery, is represented in Fig. 325. A number of lead cathode plates covered with a deposit of lead in spongy condition are joined by a crossbar, as shown at A. An equal number of lead plates covered with lead dioxide (PbO_2) are similarly joined to the bar B. These two sets of plates are arranged in the electrolyte of sulfuric acid in such a way that the plates alternate with each other but do not touch. The electromotive force of this battery is about 2 v.

The reaction at the lead plate, when the cell is being discharged, is as follows:

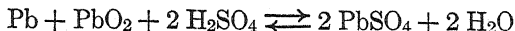


The insoluble lead sulfate deposits in the spongy lead and the two electrons are given up to the plate.

At the lead dioxide plate the reaction is



Lead sulfate deposits on the dioxide plate, and two electrons are taken from the plate. The electrons deposited on the cathode flow through the connecting wire to supply the loss at the anode. When the connection is broken, the action ceases. The complete chemical equation is



As the cell delivers current, the two electrodes approach an identical condition by deposit of lead sulfate on both. At the same time sulfuric acid is withdrawn from the electrolyte, which in consequence diminishes in density. The cell should never be allowed to discharge completely, and on reversing the current (charging the cell) the original condition of the electrodes and the electrolyte is restored.

Electroplating. An electrolytic cell is used in the important process of *electroplating*. The object of this process is to cover the surface of a metallic article with a thin coating of a second metal either as a protection against corrosion or to improve its appearance. A salt of the metal to be deposited is the electrolyte in water solution; and if it gives simple metallic ions, they are deposited on the cathode. The article to be plated is used as the cathode, and the

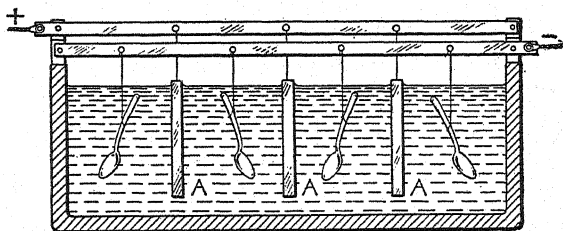


FIG. 326. Silver Plating

The article to be plated is made the cathode, plates of silver (A) the anode, and a soluble silver salt the electrolyte

current is passed through the electrolyte until a covering of the desired thickness is produced (Fig. 326). Metals high in the electro-motive series cannot be deposited from an aqueous solution under any ordinary conditions.

The metal may be deposited in the form of a closely adhering layer or a porous powder or a growth of crystals. These variations

depend on many factors, including the nature of the metal, the electrolyte used, the temperature, the concentration, the relative surfaces of the electrodes (current density), the intensity (voltage), and the rate of deposit. In any given case, conditions must be varied until the desired result is secured. Oftentimes the presence of foreign materials called *addition agents* has a very desirable effect.

Electroforming. In some cases it is desired to build up a complete object by electrolytic deposit rather than merely to cover a surface. This is called *electroforming*. An interesting application of the process is the restoration of badly corroded archaeological metallic objects to something like their original form.

A more familiar example is the process of *electrotyping*, by which the plates from which these pages were printed were made. The page is first set up in type. The face of the type is pressed into wax until a clear impression is obtained. The impressed side of the wax is coated with graphite, and this is made the cathode in an electrolytic cell containing a copper salt in solution. The copper is deposited as a thin sheet upon the letters in wax and, when detached, is a perfect copy of the type. Since the underpart of the letters is hollow, the sheet is strengthened by pouring on the undersurface a suitable amount of commercial lead. The sheet so strengthened is then used in printing.

Electrometallurgy. In electrometallurgy the electric current may be used either as a means for refining a crude metal or for the reduction of the metal from its compounds.

In *electrorefining* the crude metal is used as one of the electrodes (usually the anode) and a thin plate of the pure metal as the other electrode, with a suitable salt of the metal as the electrolyte. In copper-refining the anode plates sometimes weigh as much as 400 lb each. A low-voltage current from a dynamo is passed through the cell in such a way that the crude metal anode passes into solution as ions and is plated on the pure metal cathode. The main difficulty is to secure conditions that will leave all impurities either in solution in the electrolyte, or as a precipitate, or unchanged on the crude anode, and so will prevent any second metal from depositing on the pure cathode. Each impure metal presents a different problem. In many cases valuable materials may be recovered from the anode sludges.

In *electroreduction* various plans are followed. If the metal is not too high in the electromotive series, so that it will not decompose water, we may proceed as in the case of zinc. Zinc ores are often leached out with an acid,—usually sulfuric acid,—and the aqueous

sulfate solution is then electrolyzed with a pure zinc cathode. When the electrolyte becomes too acid, it is used to leach a new lot of ore.

With metals that decompose water rapidly, such as sodium and calcium, we must resort to the electrolysis of a *fused* electrolyte. When the elaborate structure of a crystal goes to pieces by being heated, a structureless liquid results, made up very largely of ions. Such a liquid is a good electrolyte, and from it the metal can be deposited by electrolysis, as we have seen in the case of sodium (p. 282). Because of relatively low melting points, the hydroxide or chloride of the metal is usually employed. More rarely some suitable compound of a metal is *dissolved* in one of its fused salts, so that the electrolysis is more like that of an aqueous solution. We shall find this to be the case with aluminum.

The electrolysis of a fused salt presents many practical difficulties. Necessarily the operation is carried on at a moderately high temperature, and the metal liberated is likely to be liquid and very active. It is difficult to protect it from the oxygen and nitrogen of the air. A fused salt is very corrosive and will soon destroy almost any material of which the cell walls are constructed. The oxygen or chlorine evolved at the anode is also very active and must be kept away from the depositing metal. It is because of details such as these that the electrometallurgy of each metal requires its own form of apparatus. The actual liberation of the metal usually presents no great difficulty. There is therefore room for great inventive skill in the design of apparatus to fit each particular case.

Electrothermal processes. In addition to its function as an electrolytic agent, the electric current is frequently used in metallurgy merely as a source of heat. A furnace is so constructed that it presents resistance to the current and dissipates the electrical energy into heat. These are *electrothermal* processes. In the electrolysis of fused electrolytes, the current is sometimes used in a double capacity — to electrolyze the salt and to supply heat to melt it.

Questions

1. (a) Explain why the density of the fluid in a lead storage battery is tested occasionally to determine whether the battery is sufficiently well charged. (b) Would this test always necessarily be adequate?
2. (a) It has been found possible to electroplate a metal surface with *brass*. Explain how this can be done. (b) It is also possible to electroplate with *rubber*. Explain.
3. Describe the construction and operation of a dry cell.

Problems

1. (a) If 1 coulomb of electricity will deposit 0.0011183 g of silver, calculate the number of coulombs required to deposit 1 g-equiv of silver. (b) What is the weight of this amount of silver in grams? (c) How many coulombs are there in a faraday?

2. Calculate the weight in grams of the following ions which would be deposited from their solutions by 0.05 faraday: Ag^+ , Cu^+ , Cu^{++} , Al^{+++} , Au^+ , Au^{+++} .

3. If a current of 0.1 amp passes through an aqueous sodium chloride solution for 10 minutes, what *weight* of chlorine gas would be liberated at the anode?

4. How long must a current of 1 amp be passed through acidulated water in order (a) to produce 1 l of *dry* hydrogen gas, measured at 27° and 745 mm; (b) to produce 1 l of hydrogen at 27° and 745 mm but collected *over water*?

5. When a current of 1 amp is flowing through a wire, how many electrons pass a given point on the wire per second?

6. If a Daniell cell operates just long enough to allow 1 g-equiv of zinc to dissolve at the negative electrode and 1 g-equiv of copper to deposit at the positive electrode, how much electrical energy is furnished by the cell if the voltage is 1.10?

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CHAPTER 32

The Very Active Metals and Their Compounds

ELEMENT	ATOMIC WEIGHT	ATOMIC NUMBER	DENSITY	MELTING POINT	ELECTRONS IN SHELLS
Lithium	6.940	3	0.53	186.0°	2:1
Sodium	22.997	11	0.97	97.5°	2:8:1
Potassium	39.096	19	0.86	62.3°	2:8:8:1
Rubidium	85.48	37	1.53	38.5°	2:8:18:8:1
Cesium	132.91	55	1.90	26.0°	2:8:18:18:8:1
Calcium	40.08	20	1.55	810.0°	2:8:8:2
Strontium	87.63	38	2.6	800.0°	2:8:18:8:2
Barium	137.36	56	3.5	850.0°	2:8:18:18:8:2

Introduction. The elements listed in this table are the *very active metals*, and all fall in the A families of Groups I and II in the periodic table. The first five metals in the list have long been called the *alkali metals* because of the strong alkaline character of their hydroxides. Similarly, the last three have been called the *alkaline-earth metals* because their oxides seemed to lie between the hydroxides of the alkali metals and the oxides of the earth metals (magnesium, aluminum, iron) in chemical properties. For reasons that will appear as we go along, the other members of these periodic families are not considered in this chapter. Radium has been studied in an earlier chapter; beryllium, magnesium, zinc, and cadmium will be taken up in the next chapter; and mercury will be deferred until we reach some of the inactive metals.

The metals of the group. Of the metals named in the table, sodium and potassium were first prepared in the free state by Humphry Davy in 1807 (Fig. 190). In the following year he succeeded in isolating very small samples of calcium, strontium, and barium. Lithium, rubidium, and cesium were first isolated by the German chemist Bunsen (by electrolysis), lithium in 1855 and the others in 1860-1861.

Occurrence of the metals. Calcium, sodium, and potassium, in the order named, rank immediately below iron in abundance in the earth's solid crust and in the oceans; calcium comprises 3.39 per

cent and potassium 2.40 per cent. Apparently the alkali metals were originally present largely as complex silicates, and in the weathering processes of nature the sodium silicates were decomposed more rapidly, so that sodium passed into solution as ions of simple salts, such as the chloride or the sulfate. Accordingly sodium (as chloride) is much more abundant in sea water and in salt deposits than is potassium; and potassium, as well as the rare elements lithium, rubidium, and cesium, is found more largely in unchanged silicates.

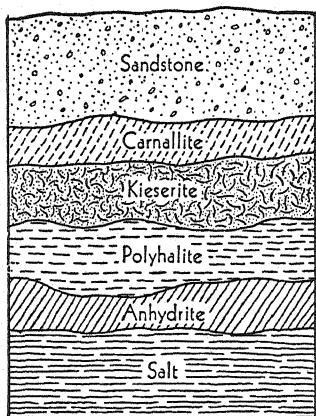


FIG. 327. *Cross-section Diagram of the Stassfurt Salt Deposits*

However, potassium compounds of relatively simple character are always present in fertile soils, and traces of lithium and even rubidium and cesium may be present in soils that have been formed by the weathering of silicate rocks containing these rare elements.

Lithium and rubidium, like potassium, may be absorbed by certain plants, and have been detected in the ashes of tobacco, coffee, and beets. Vast beds of soluble sodium salts are found in many countries, and, to a much less extent, beds of potassium salts. Nearly all these have been deposited from salt water in past ages. To some extent lithium, rubidium, and cesium are present in deposits of potassium salts; but their chief source is the minerals lepidolite and amblygonite, which, in this country, are found most abundantly in South Dakota and California. Lithium phosphate is found in Texas, and the brines of Searles Lake in California are yielding large quantities of lithium salts.

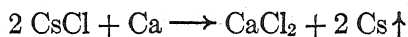
Calcium, strontium, and barium occur almost wholly in deposits of more or less pure carbonate and sulfate, with less available percentages in various other minerals, chiefly silicates and phosphates.

Stassfurt salts. These salts, evidently deposited from sea water under peculiar geological conditions, form very extensive deposits in middle and northern Germany. The most noted locality for working them is at Stassfurt. The deposits are very thick and rest upon an enormous layer of common salt. They are in the form of a series of strata, each consisting largely of a single mineral salt. Over thirty different minerals are present, but some are in very small quantities. Fig. 327 shows a cross section of these deposits. Since the strata differ in general appearance, they can be

mined separately; and each mineral can be worked up by methods adapted to it. The chief minerals of commercial importance in these deposits are the following:

Sylvite	KCl	Kainite	$\text{MgSO}_4 \cdot \text{KCl} \cdot 3 \text{H}_2\text{O}$
Anhydrite	CaSO_4	Kieserite	$\text{MgSO}_4 \cdot \text{H}_2\text{O}$
Carnallite	$\text{KCl} \cdot \text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$	Schönite	$\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 6 \text{H}_2\text{O}$
Halite	NaCl	Boracite	$2 \text{Mg}_3\text{B}_5\text{O}_{15} \cdot \text{MgCl}_2$
Polyhalite			$\text{MgSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 2 \text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$

Production of the metals. All the metals of this group are produced by the electrolysis of fused electrolytes, usually the chloride, less often the fluoride or mixtures of the chloride and fluoride. The electrolysis of melted sodium chloride has been described (p. 282). The only other ones produced in commercial quantities are calcium and barium. These present difficulties in that their chlorides melt at a relatively high temperature, and the deposited metal tends to migrate into the liquid electrolyte as a kind of colloidal dispersion, and so must be removed from the cell as fast as deposited. Special forms of cells are necessary for each metal of the group. Fig. 328 shows the form of cell used for the production of calcium. Because of the easy volatility of cesium, this metal is best obtained by distilling the chloride with metallic calcium:



Characteristics of these metals.

We think of a metal as a rather heavy material, but most of these metals are very light. Even barium, the heaviest of the eight under consideration, is less than half as heavy as iron. The alkali metals are all very soft and have low melting points; the alkaline-earth metals are much harder (calcium is the hardest) and melt at nearly the same but much higher temperature. All have silvery

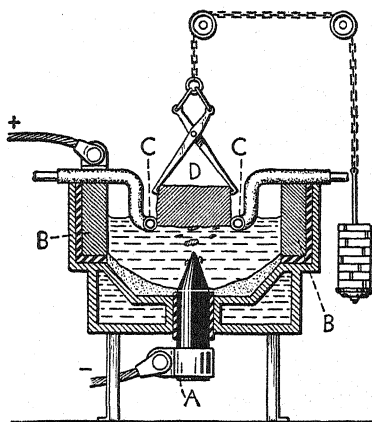


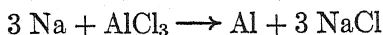
FIG. 328. *Electrolytic Cell for the Production of Calcium*

The cell consists of a cylindrical vessel through the bottom of which extends an iron cathode A. The anodes B, B, several in number, are distributed about the sides of the vessel. The calcium separates at the cathode as a liquid and rises in the form of globules to the lower surface of a solid stick of calcium D, suspended above the cathode, as shown in the diagram. There it becomes chilled by a water-cooling device C, C and adheres to the stick of calcium, which is slowly raised as it increases in length.

luster and are good electrical conductors, but they are not very malleable or ductile and have little strength.

As may be seen in the table on page 569, the atoms of all the alkali metals have but one valence electron, and in all their compounds they are univalent; the atoms of the alkaline-earth metals each have two valence electrons, and in their compounds they are bivalent. In a very few, such as the subchloride CaCl , they are univalent. These metals are all exceedingly active. They stand at the head of the electromotive series, and decompose water at ordinary temperatures with evolution of hydrogen. The alkaline-earth metals are less active than the alkali metals, but all of them are powerful reducing agents. They all oxidize rapidly in the air, and lithium and the alkaline-earth metals readily combine with nitrogen to form nitrides.

Uses of the metals. Metallic sodium was first prepared in quantity for the early production of aluminum from the chloride:



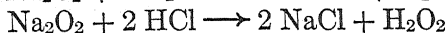
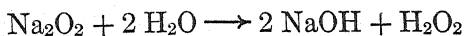
It is now produced by the ton and sold in large bricks or even in tank-car lots. It is used in the manufacture of sodium cyanide (insecticide and electrolytic baths), lead tetraethyl (antiknock), dyes and various other organic compounds, and sodium peroxide. To some extent it is used to purify certain alloys and other metals. The chief use of the rare metals rubidium and cesium depends upon the ease with which they emit electrons under the influence of light (of ordinary wave lengths). In the form of a very thin film, only a few atoms thick and deposited on the surface of a supporting metal, they are the essential part of photoelectric cells and thermionic tubes for radio work.

Calcium has uses as a reducing and purifying agent in the metallurgy of a number of metals and would have a wider use if it could be produced at a lower cost. Both calcium and barium are constituents of bearing-metal alloys to harden softer metals. Metallic lithium, potassium, and strontium have no uses not supplied by other metals of this group.

Oxides of the metals. None of the oxides of these metals occurs in nature; and the oxides of only two of them, sodium and calcium, have present industrial importance, though of course the oxides of all the others can be made. Barium peroxide, BaO_2 , was formerly used in preparing oxygen and hydrogen peroxide, but it has ceased to be very important.

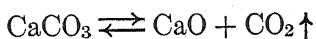
Oxides of sodium. If sodium is burned in a limited supply of oxygen at a controlled temperature, the expected (valence) oxide Na_2O can be prepared. It is a white powder and is a very powerful drying agent. In combining with water it can be made to form anhydrous sodium hydroxide. It attacks many substances both inorganic and organic, and is a newcomer in the group of powerful chemicals.

If the metal in the form of shavings is burned in an abundant current of air, the peroxide, Na_2O_2 , is formed. Treated with water or dilute acids it yields hydrogen peroxide:



Sodium peroxide is an important source of hydrogen peroxide, as well as of many other peroxides, peracids, and salts, such as perborates and percarbonates. All these compounds are strong oxidizing agents.

Calcium oxide (lime) (CaO). Calcium oxide, known also as *lime* or *quicklime*, is obtained commercially by heating limestone (CaCO_3) in large furnaces, or *kilns*:

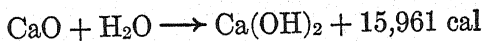


The pure compound can be prepared by heating pure calcium carbonate or nitrate.

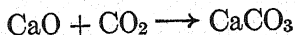
The decomposition of calcium carbonate is reversible. If the reaction is carried out in a closed vessel, equilibrium between the opposing reactions is reached at any definite temperature when the dissociation pressure reaches a definite value characteristic for that temperature (p. 338). The higher the temperature, the greater is the pressure at equilibrium.

If, on the other hand, the carbon dioxide is conducted away as fast as formed, the decomposition will continue until complete. This is the method adopted in the production of lime, for the limestone is heated in a current of air, which carries away the carbon dioxide.

Pure calcium oxide is a white amorphous substance whose density is about 3.4. When heated intensely in the oxyhydrogen blowpipe, it gives a brilliant light. It has a high melting point (2572°) and boils vigorously (2850°) when heated in an electric furnace. It acts upon water with the evolution of considerable heat (whence the name *quicklime*, or "live lime"), and the process is called *slaking*:



It also absorbs carbon dioxide from the air and forms the carbonate:



Lime exposed to air is therefore gradually converted into the hydroxide and the carbonate and will no longer slake with water. It is then said to be *air-slaked*. Lime is produced in nearly every state, although Ohio and Pennsylvania lead in the production. Its greatest use is in the preparation of calcium hydroxide, largely employed in building construction. It has many other uses, as in the reduction of metals (especially iron) from their ores, and in the manufacture of glass, of paper, and of calcium carbide, from which acetylene is prepared. For many of its uses lime is slaked, or converted into the hydroxide, during its use.

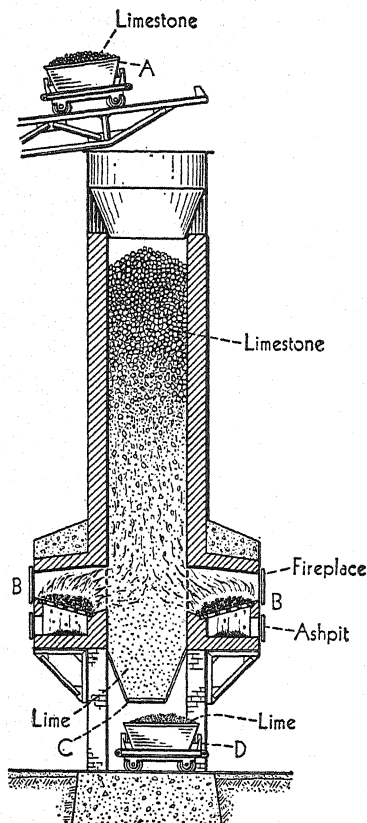
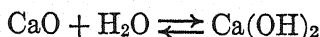


FIG. 329. A Vertical Section of a Limekiln

Commercial production of lime. Lime is made by heating limestone in large, chimneylike furnaces called *limekilns*. A vertical section of a modern limekiln is shown in Fig. 329. The kiln is about 50 ft in height. The fireboxes, or furnaces (*B, B*), are built around the lower part, and lead into the central stack. Limestone is added at the top of the kiln, as shown at *A*. The hot gaseous products of combustion are drawn up through the kiln, and the limestone is gradually decomposed by the heat. The bottom of the furnace is so constructed that a current of air is drawn in at *C*.

This cools the hot lime at the base of the furnace, furnishes heated oxygen for the combustion, and removes the carbon dioxide from the kiln. The lime is dropped into cars *D* run under the furnace. Usually several of these kilns are operated together.

Calcium hydroxide (slaked lime) ($\text{Ca}(\text{OH})_2$). This important compound results when lime is treated with water:



The reaction is reversible, and the oxide can be obtained from the hydroxide by heating the latter above 450° in an open vessel. As

usually prepared, it is a white powder, though under proper conditions it can be crystallized from water in glittering crystals of the formula $\text{Ca}(\text{OH})_2 \cdot \text{H}_2\text{O}$. It is very sparingly soluble in water, and its solubility diminishes with rise in temperature. At 10° , 1 l of water dissolves 1.76 g of the hydroxide; at 50° , 1.28 g; and at 100° , only 0.77 g.

Its solution in water is called *limewater* and is often used in medicine because of its basic properties. Because of its low cost calcium hydroxide is much used in the industries whenever a mild alkali is desired. It has a wide variety of uses, the most important of which are as follows: in the manufacture of various building materials, such as mortar, plaster, stucco, and like products; in the softening of water; in the manufacture of insecticides, such as the lime-sulfur sprays (p. 356); in the preparation of bleaching powder and of the hydroxides of sodium and potassium; for agricultural purposes, especially for neutralizing the acid in sour soils; in purifying coal gas; and in removing the hair from hides in the manufacture of leather.

Mortar; plaster; stucco. Ordinary mortar consists of a mixture of calcium hydroxide, sand, and water. When exposed to air, the water is absorbed or evaporates, and the mortar gradually hardens, or sets. In this process the calcium hydroxide is slowly acted upon by the carbon dioxide in the air, forming calcium carbonate. At present cement (chap. 34) enters largely into the composition of mortars.

Formerly, the plaster applied to interior walls of buildings consisted of a mixture of calcium hydroxide, sand, and hair or wood fiber. At present various manufactured products are used in which plaster of Paris is the principal constituent. Plasters applied to the exterior of buildings are called *stucco*. They consist of sand or other filler together with a binding material. Formerly the binder was always a paste of lime, though in modern practice cement is generally mixed with the lime. Colored sand or added coloring materials afford a wide range of color, and the coating is very durable if the understructure is good. The stucco may be applied to almost any kind of strong surface, and the use of this material is rapidly increasing in this country.

Lime-stucco plasters have been used from the earliest days, dating back to Mesopotamia in 3500 B.C. They were much used by Egyptians, Greeks, Romans, and Moors in their best periods of architecture. In 1505 Raphael examined the Golden House of Nero and as a result revived the use of hard stucco in Italy. Thence its use spread widely into most European countries, and many of their finest architectural monuments are stucco-covered.

The carbonates. By far the most important carbonates of this group of metals are those of sodium and of calcium. Lithium carbonate, Li_2CO_3 , is the only nearly

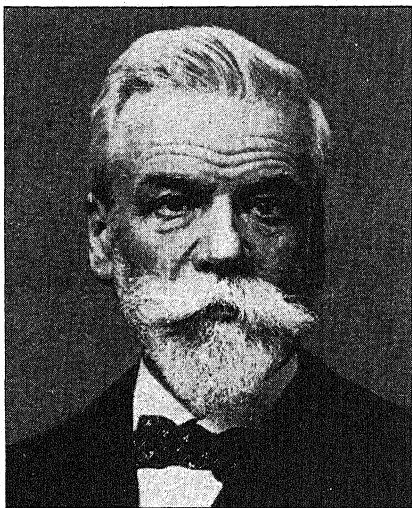


FIG. 330. Ernest Solway (1835–1922)

A famous Belgian chemical engineer who developed the Solway process for the manufacture of sodium carbonate

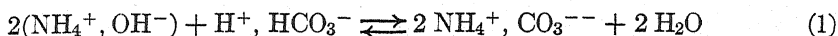
insoluble carbonate of the alkali metals and is one of the salts whose precipitation brings about a separation of lithium from the other alkalies. All other lithium salts can be prepared from this carbonate. It has come into wide use in making special kinds of glass and glazes and is replacing the mineral lepidolite, formerly used to add lithium to these products. The carbonate of potassium, K_2CO_3 , resembles sodium carbonate closely. It is a useful laboratory reagent, but has few industrial uses, the chief one of which is in the manufacture of hard glasses. The carbonates of strontium, SrCO_3 (strontianite), and of barium, BaCO_3 (witherite), are valuable

minerals for the production of other compounds of these two metals. They are not abundant minerals, and the mineral sulfates, though not so desirable, are used instead.

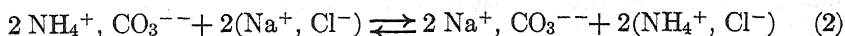
Sodium carbonate (soda ash) (Na_2CO_3). This very important compound has long been almost entirely a manufactured salt. Many years ago it was obtained by burning seaweeds, some of which are rich in compounds of sodium. When the weeds are burned, the resulting ashes contain the sodium as carbonate, which accounts for the name *soda ash*. In a similar way land plants and trees build up potassium compounds in their structures, and their ashes yield potassium carbonate. In more recent years sodium carbonate has been found to be a constituent of the salts of dried-up desert lakes, particularly of Searles Lake and Owens Lake in California. These deposits are worked for a number of salts, such as borax, potassium salts, sodium sulfate, and compounds of lithium. Along with these, sodium carbonate is recovered to the extent of about 100,000 tons annually. Deep borings (300 ft) at Searles Lake disclose unexpected and enormous deposits of both sodium carbonate and the bicarbonate.

The manufacture of sodium carbonate. As a manufactured salt, the sodium carbonate used in the United States is made from sodium chloride, nearly all by a process devised by the Belgian chemical engineer Ernest Solvay (Fig. 330) and known as the *Solvay process*. In this process ammonia and carbon dioxide are passed into a concentrated solution of sodium chloride, with the formation of ammonium carbonate, which then reacts with the sodium chloride to form the sparingly soluble sodium bicarbonate. This bicarbonate precipitates, is removed by filtration, and is changed into the normal carbonate by heating.

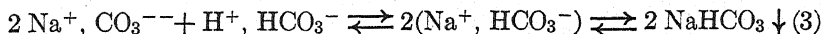
Reactions involved in the Solvay process. The ammonia and carbon dioxide passed into the solution of sodium chloride first react with water to form ammonium hydroxide and carbonic acid respectively; these then react to form ammonium carbonate:



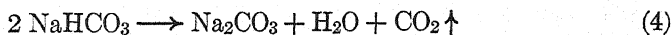
The ions of the resulting ammonium carbonate then react with the sodium chloride to form sodium carbonate:



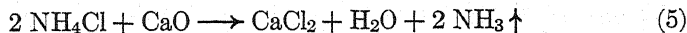
The sodium carbonate formed is quite soluble and remains in solution. As more carbon dioxide is passed into the solution the sodium carbonate is changed into the less soluble bicarbonate, which precipitates:



The bicarbonate is removed by filtration and changed into the normal carbonate by heating:



The "mother liquors" remaining after the precipitation of the sodium bicarbonate contain ammonium chloride formed according to equation (2). These are treated with lime (CaO) to liberate the ammonia for use once more:



The lime is obtained by heating limestone (CaCO_3):



The ammonia liberated according to equation (5) and the carbon dioxide liberated according to equation (6) are used in preparing more ammonium carbonate (equation (1)). Theoretically the ammonia used in the process is all recovered (equation 5) and so can be used over and over again, but of course there is some unavoidable loss.

Properties and uses of sodium carbonate. The aqueous solution of this salt is alkaline in character because of hydrolysis (p. 372). The salt forms a number of hydrates, the most common of which is the decahydrate $\text{Na}_2\text{CO}_3 \cdot 10 \text{H}_2\text{O}$. By cooling a hot solution of the carbonate this hydrate is obtained in the form of large, clear, monoclinic crystals and is often known as *washing soda*, or *sal soda*.

The decahydrate effloresces on exposure to dry air, changing into the monohydrate. The anhydrous salt melts at 851° and along with potassium carbonate is used for decomposing silicates. Mere mention of the fact that sodium carbonate is used in the manufacture of glass, soap, various other cleansers, and many chemical reagents will indicate its importance in the industries. About 2,000,000 tons is produced annually in the United States for these various uses, and nearly all the manufactured salt is made by the Solvay process.

Sodium hydrogen carbonate (bicarbonate of soda, or baking soda) (NaHCO_3). This salt is made either by the Solvay process, as already explained, or by passing carbon dioxide into saturated solutions of sodium carbonate:



When the solid is heated, the reaction is reversed, and the bicarbonate changes into the carbonate with liberation of carbon dioxide. The salt is used as an aerating agent in baking. For this purpose it is mixed with some substance, such as sour milk, cream of tartar, or an acid phosphate (see baking powders), that slowly reacts with the carbonate and liberates carbon dioxide.

Calcium carbonate (CaCO_3). Enormous quantities of calcium carbonate occur in nature. *Limestone* is the most abundant form. It is a grayish rock that is usually found in hard, stratified masses. Whole mountain ranges are sometimes made up of this material or of the double compound $\text{CaCO}_3 \cdot \text{MgCO}_3$ (dolomite). Limestone is never pure calcium carbonate, but always contains variable percentages of foreign matter, usually magnesium carbonate, clay, silica, compounds of iron and aluminum, and frequently fossil remains. *Marl* is a mixture of limestone and clay. *Pearls, coral*, various kinds of *shells* (such as eggshells and oyster shells), and *natural chalk* (not the blackboard crayon) are largely calcium carbonate.

The more usual form of crystalline calcium carbonate belongs to the hexagonal system; and *calcite* is a nearly pure example of this form. Very beautiful transparent crystals of calcite are found in Iceland, and the name *Iceland spar* is often given to this variety

(Fig. 331). *Mexican onyx* is a massive variety, streaked or banded with colors occasioned by impurities. *Marble* is made up of minute calcite crystals, and was probably formed by the crystallization of the melted rock under great pressure. *Stalactites* and *stalagmites* are icicle-like forms sometimes found in caves. Calcium carbonate is also found in nature in the form of crystals belonging to the rhombic system. The mineral *aragonite* is an example of this form. When heated it is transformed into a mass of calcite crystals. This transition is probably taking place at ordinary temperatures but with a very low speed; so it is easy to understand why the aragonite form is a rather uncommon variety.

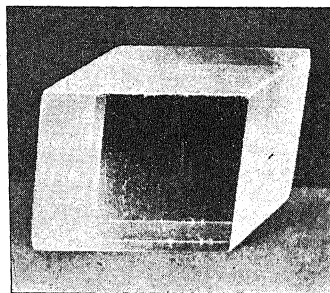
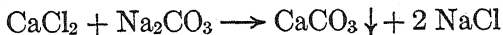


FIG. 331. A Crystal of Iceland Spar

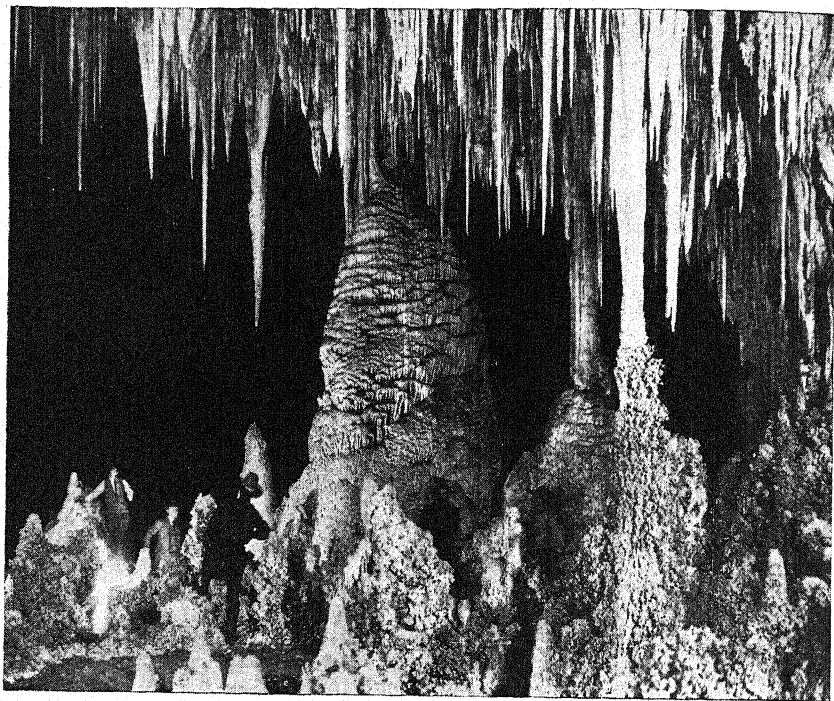
Production and uses of limestone. Limestone is mined in all but three or four of the states (nearly 100,000,000 tons annually); Ohio, Illinois, Pennsylvania, New York, and Michigan, in the order named, lead in the production of broken stone for all technical purposes. More than half is used in the construction of roads and in making concrete. Large amounts are utilized as a flux in separating metals from their ores, and, in powdered form, for neutralizing the acid present in certain soils. It is the source of all commercial lime and, in addition, has numerous minor uses. In large quarried blocks, it is our principal building stone.

Preparation of pure calcium carbonate. In the laboratory pure calcium carbonate can be prepared by precipitation:



When the precipitation takes place at ordinary temperatures, the carbonate is obtained in the form of exceedingly small calcite crystals. If the carbonate is precipitated from hot dilute solutions, aragonite crystals are obtained, but these slowly change into the calcite form.

Pure calcium carbonate is very slightly soluble in water; 1 l of water at 15° dissolves but 13 mg, or, if it is in the form of aragonite, 15 mg. The action of acids upon the carbonate, as well as the effect of heat upon it, has already been described. Precipitated calcium carbonate is the basis of many tooth powders and polishing powders.



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FIG. 332. *View in the Carlsbad Caverns, Showing Stalactites and Stalagmites*

Calcium acid carbonate (calcium bicarbonate) ($\text{Ca}(\text{HCO}_3)_2$). While calcium carbonate is almost insoluble in pure water, it readily dissolves in water containing carbon dioxide. This is due to the formation of the soluble but unstable calcium acid carbonate. When solutions containing the acid carbonate are heated, the normal carbonate is precipitated :



Natural waters always contain more or less carbon dioxide in solution. In the case of certain underground waters the amount of carbon dioxide is comparatively large, since it is held in solution by pressure. Such waters have a marked solvent action upon limestone, dissolving both the calcium carbonate and the magnesium carbonate. In certain localities this solvent action, continued through geological ages, has resulted in the formation of large caves in limestone rock, such as the Mammoth Cave in Kentucky and the Carlsbad Caverns in New Mexico (Fig. 332).

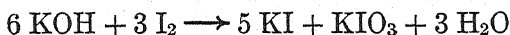
The halogen compounds of the group. Of the chlorides of the alkali metals, *sodium chloride* is by far the most abundant and im-

portant, and has already been described in Chapter 17. Thick strata of relatively pure salt underlie hundreds of square miles of surface in various parts of the world, and recrystallization of the crude salt yields a sufficiently pure compound. As has been explained, it is the source of both the sodium and the chlorine of nearly all the great variety of the compounds of these elements that are so necessary for civilization. Salt itself is necessary to all animal life, both to supply the essential sodium ion, and to furnish the hydrochloric acid required in the process of digestion.

Potassium chloride, KCl , also occurs in many salt beds either as the chloride itself (sylvite) or more often combined with magnesium chloride as the mineral carnallite, $\text{KCl} \cdot \text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$. As with the sulfate, its chief use is as a fertilizer, but it is also the source of nearly all manufactured chemicals containing potassium.

Lithium chloride, LiCl , has come into prominence in connection with air-conditioning, since there is now an assured production. Concentrated solutions of this very soluble salt have a low vapor pressure, and air bubbled through such a solution has about the right humidity for comfort (about 50 per cent at 70°).

The *bromides* and *iodides* of *sodium* and *potassium* have uses as drugs and in photography. They are usually made (by similar reactions) by treating a solution of the hydroxide with the free halogen, thus:



The iodate (or bromate) can then be reduced to the simple halogen salt by heating it or by a reducing agent.

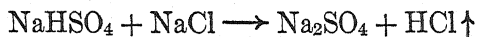
The human body contains about 50 mg of iodine, one fifth of which is in the thyroid gland, and this small amount seems to be essential to health. For example, at least one form of *goiter* (enlargement of the thyroid gland) is thought to be due to a lack of iodine. As a rule, our foods contain sufficient iodine to meet our needs. To guard against any lack of the element, our grocers sell a grade of salt that contains a minute percentage of potassium iodide; but this product should not be used except on the advice of a physician, since too much iodine may prove as harmful as too little.

Apart from minor uses as chemical reagents and in the production of the free metals, *calcium chloride* is the only halide of the alkaline-earth metals that has important uses. Crystallized from water, it forms the extremely soluble hydrate $\text{CaCl}_2 \cdot 6 \text{H}_2\text{O}$, but the anhydrous chloride, CaCl_2 , is often used as a drying agent because it has

a great tendency to recover at least some of its water of hydration. Calcium chloride is a by-product in certain industries (see Solvay process) and in the recovery of more valuable salts from salt deposits. From the latter source it is usually found mixed with the very similar magnesium chloride. It owes its uses to its great solubility. It makes a suitable brine for the manufacture of ice, and many tons of it are used to spread on highways, tennis courts, the walls of mines, and similar dusty places to lay the dust. The chlorides of strontium and barium have uses as laboratory reagents.

Calcium fluoride, CaF_2 , is an insoluble mineral (fluorspar) used as a flux in metallurgy, as a component of the electrolyte in some electrolytic cells, and as the source of fluorine for all its compounds.

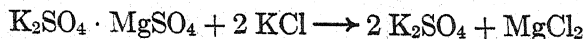
The sulfates. Of the sulfates of the alkali metals only those of sodium and potassium are of industrial importance. Formerly *sodium sulfate* was obtained as a by-product in the preparation of hydrochloric acid from salt and nitric acid from Chile saltpeter (pp. 291, 384). Both these processes produce the bisulfate, NaHSO_4 , called salt cake, which is converted into the normal sulfate by heating with salt:



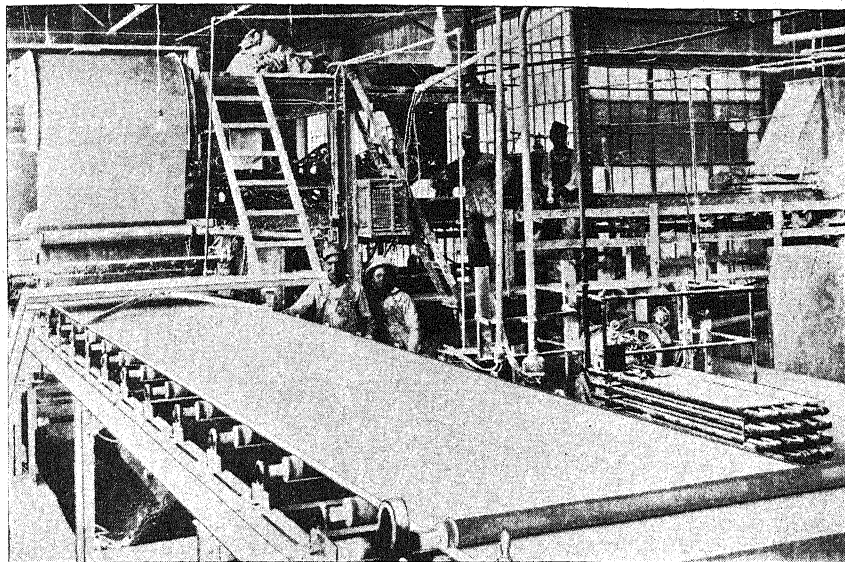
To meet a growing demand, new sources have been sought and found in the great salt beds in a number of Western states, and about 80,000 tons of sodium sulfate are being produced annually from this source. The chief uses of sodium sulfate are in the manufacture of rayon, glass, and wood pulp and paper.

Below 32.38° sodium sulfate crystallizes from solution as the hydrate $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$. This compound is called *Glauber's salt* from the alchemist Glauber, who lived about the middle of the seventeenth century, and who first used the compound in medicine—a use that still continues. At temperatures above 32.38° the anhydrous salt crystallizes from solution, and the transition temperature from the anhydrous salt to the hydrate is so definite that it has been used in the calibration of thermometers.

Potassium sulfate, K_2SO_4 , can be made by the action of sulfuric acid on potassium chloride, but commercially it is made from double salts found in salt deposits, especially from *schönite* from the salt mines of Stassfurt, Germany—a salt which has the formula $\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4$. The equation is



It is used as a fertilizer and for making potassium aluminum sulfate,



Certainteed Products Corporation

FIG. 333. Gypsum-Board Mill

or potash alum. Heated with sulfuric acid, it gives *potassium bisulfate*, which has some uses as a reagent.

Sulfates of the alkaline-earth metals. These sulfates are all nearly insoluble in water and are colorless or white minerals. Calcium sulfate is the most soluble one.

Calcium sulfate, CaSO_4 , occurs in salt deposits in anhydrous form as the mineral *anhydrite*. In massive rocklike form — sometimes as smaller individual crystals — it is found as the hydrate $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, called *gypsum*. There are special forms of gypsum called selenite, alabaster, and satin spar. Of these various forms, gypsum is by far the most important and is mined in very large tonnages. Our supply comes chiefly from New York, Michigan, Iowa, and Texas and to a less extent from other states; considerable quantities are imported from Canada.

Gypsum has many important uses, although the building trades take the most of it. The crushed and pulverized rock is heated to drive off most of the water of hydration, and is mixed with such filling material as shredded asbestos, mineral wool, hair, shavings, sawdust, and often dextrin. It is moistened and molded or pressed into the form of lath, wallboard, tile, and similar supplies (Fig. 333). As the gypsum recovers its water of hydration, these articles become as rigid as wood, and are fireproof. Ground gypsum is also used in

cement to retard its setting, as a paint pigment, and as a fertilizer for certain types of soils.

Plaster of Paris (or gypsum plaster) is a white powder made by dehydrating gypsum at about 125° until it reaches the approximate composition $(\text{CaSO}_4)_2 \cdot \text{H}_2\text{O}$. When moistened, it forms a plastic mass that can be molded into any desired shape; and as the water of hydration is recovered, the mass expands slightly and sets to a hard stonelike state. These properties make it very useful for casts of various kinds, for stucco work, for cementing glass to metals, and for a finishing coat on plastered walls.

A form of very specially prepared and partially dehydrated gypsum has been given the trade name *Dryerite*. It is very efficient in absorbing moisture from gases of all kinds.

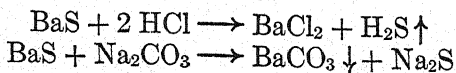
The sulfates of strontium and barium. Of these two, strontium sulfate, SrSO_4 , is the less important. As a mineral it is called *celestite*. At Put in Bay (Ohio) beautiful large crystals of celestite line the walls of Strontia Cavern, and other deposits are found in various localities. As a mineral, barium sulfate, BaSO_4 , is called *barite*, or *heavy spar*. In this country it is produced chiefly in Missouri and Georgia, but also in half a dozen other states. Since these two sulfates have been more abundant than the carbonates, salts of the two metals are usually made from the sulfate and by similar methods. There is, however, little demand for salts of strontium.

A large fraction of the barite mined in this country is put to a singular use that depends almost wholly on its high density (3.4–4.6). It is ground up and put into oil wells that have high gas pressures. Mixed with the water and oil in the well, it forms a heavy layer in the bottom of the well that helps to prevent the escape of gas. A second use of the purified sulfate is in the X-ray photography of the digestive tract. A material is opaque to X rays in proportion to its density. To have his digestive tract X-rayed, a patient drinks a large volume of a suspension of barium sulfate in water, and this gives the contents of the intestine sufficient opacity to make a good X-ray picture possible.

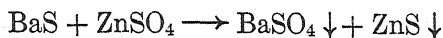
For other uses the sulfate is first reduced to the sulfide by heating it with carbon:



The sulfide is soluble in water and is easily decomposed by almost any other acid to form the corresponding salt:

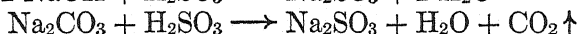


Both barium sulfate and zinc sulfide are insoluble; and if a solution of BaS is added to a solution of ZnSO₄, an interesting reaction takes place in which *two* insoluble precipitates are formed:



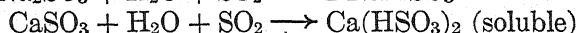
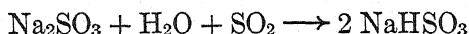
These precipitated compounds are both white, and are very intimately mixed. The mixture is known to the trade as *lithopone*, and it is an important paint pigment. Precipitated barium sulfate is also used as a pigment, under the name *blanc fixe*.

The sulfites and thiosulfates. The sulfites of the metals resemble the carbonates in formulas, methods of preparation, solubility, and in many chemical reactions. Sodium sulfite and bisulfite are soluble; calcium sulfite is insoluble, while the bisulfite is soluble. Sodium sulfite is made by the action of sulfurous acid, H₂SO₃ (SO₂ + H₂O), on sodium hydroxide or carbonate:



In the industries sodium carbonate is added to a saturated solution of sulfur dioxide in water, while calcium sulfite is made by the action of sulfur dioxide on calcium hydroxide or limestone.

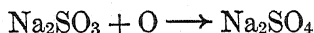
If the sulfur dioxide is in large excess, the sulfites are converted into bisulfites:



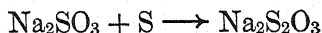
This latter equation recalls the action of carbon dioxide on limestone:



In one important respect the sulfites and bisulfites differ from the carbonates. They combine readily with oxygen to form sulfates and are *reducing* agents:



They also combine with sulfur to form salts called *thiosulfates*, the best known of which is *sodium thiosulfate*, which in crystal form is the hydrate Na₂S₂O₃ · 5 H₂O:



The chief use of the sulfites and bisulfites is in the wood-pulp industry. They dissolve the varnish-like compound (lignin) that binds the wood fibers together in solid wood. Sodium thiosulfate is used in photography and as a chemical reagent for special purposes. It is often called sodium hyposulfite, or merely "hypo."

The nitrates. The nitrates of sodium and potassium are the only nitrates found in appreciable quantities in nature, and for centuries potassium nitrate was the only source of nitric acid. Apart from these two, not many nitrates have wide uses in the industries. With the development of synthetic nitric acid the natural nitrates lost much of their former importance.

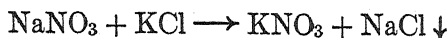


FIG. 334. *The Stamps of Chile Honor the Saltpeter Industry*

Sodium nitrate, NaNO_3 , occurs in immense deposits in the desert regions of Chile (whence the name *Chile saltpeter*, Fig. 334) and in smaller deposits in other desert places. The rock-material carrying the nitrate is mined, leached with water, and the very soluble nitrate is recovered by evaporation of the clarified solution.

Considerable quantities are still exported for fertilizers, but not to the extent of former years.

Potassium nitrate, KNO_3 (saltpeter), forms in the earth about stables and piles of decomposing refuse, and it was formerly obtained from such sources. It was one of the important reagents of the alchemists. At present it is made from sodium nitrate and potassium chloride by double decomposition in concentrated solution:



The chief use of potassium nitrate is in the manufacture of gunpowder (or black powder) and as a preservative for meat. It is a good oxidizing agent. When heated, it melts rather easily (at 333°) and decomposes into potassium nitrite, KNO_2 , and oxygen. It was by this reaction that Scheele first obtained oxygen.

The reaction employed in making potassium nitrate would seem to promise little success, since all four compounds represented in the equation are soluble in water. Its success depends on the apparently unimportant fact that sodium chloride is about as soluble in cold water as in hot water, while sodium nitrate and potassium chloride are very soluble in hot water, but not so much so in cold. Consequently when hot saturated solutions of the latter two salts are brought together, the product $[\text{Na}^+] \times [\text{Cl}^-]$ greatly exceeds the solubility product, and sodium chloride precipitates and is filtered off. This leaves the ions of potassium nitrate in solution, and the salt crystallizes from the filtrate.

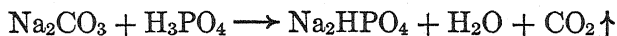
Gunpowder. Gunpowder is an intimate mixture of potassium nitrate, charcoal, and sulfur. When ignited by a spark, it burns explosively, forming a number of products, some of which are gases, while others are solids. The gases constitute about 50 per cent by weight of the total products and consist principally of carbon monoxide, carbon dioxide, and nitrogen, while

the principal solids formed are potassium carbonate, potassium sulfate, and potassium sulfide. Sodium nitrate is often used in place of potassium, but it makes a slower explosion and attracts moisture. Today the chief use of gunpowder is for blasting in coal mines and for making time fuses; in small quantities it is used as an explosive in small firearms.

The phosphates. The calcium phosphates have already been described in connection with phosphoric acid, and will be mentioned again in the discussion of fertilizers (Chap. 38). The phosphates of the alkali metals (and of ammonium) are the only soluble ones apart from some acid phosphates, and of these the sodium phosphates are the important ones.

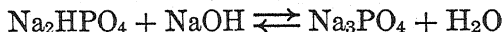
The sodium phosphates. The names and formulas of the sodium salts of phosphoric acid have already been given (p. 407).

The common phosphate used in the laboratory is the *disodium phosphate*, Na_2HPO_4 . This salt is present in our blood and urine, and it was from these sources that the compound was first obtained. It is prepared by the action of phosphoric acid on sodium carbonate:



The salt crystallizes from the solution in the form of the hydrate, $\text{Na}_2\text{HPO}_4 \cdot 12 \text{H}_2\text{O}$.

The normal *sodium phosphate*, or *trisodium phosphate*, is obtained by the action of sodium hydroxide on the disodium salt:



When the solution is evaporated, crystals that have the formula $\text{Na}_3\text{PO}_4 \cdot 12 \text{H}_2\text{O}$ separate. The aqueous solution of the salt is strongly alkaline in reaction, owing to hydrolysis. When added to hard waters, the calcium, magnesium, and iron ions are precipitated as phosphates, and the water is left alkaline in reaction; hence the use of the salt to soften hard waters in our homes and in laundries.

Monosodium phosphate is formed by the action of phosphoric acid on the disodium salt:



Sodium metaphosphate, NaPO_3 , exists in many forms, chiefly as polymers of the simple one. The sodium hexametaphosphate, $(\text{NaPO}_3)_6$, is effective in softening water.

The cyanides. Hydrocyanic acid (HCN) is one of the weakest of acids, and simple soluble salts with only the strongest of bases are known. Sodium cyanide is the most important of these.

Sodium cyanide, NaCN , is a very soluble, colorless salt and in solution is strongly alkaline because of hydrolysis. It is extremely

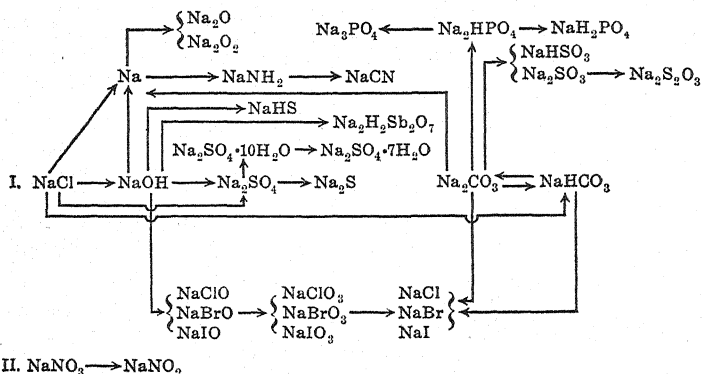
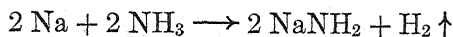


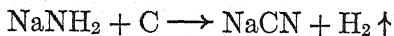
FIG. 335. Diagram Showing Steps in the Preparation of Important Compounds of Sodium, Starting with Sodium Chloride or Sodium Nitrate

poisonous, and treated with acids it evolves hydrogen cyanide, used as an insecticide, especially with citrus trees. Its solution dissolves gold and silver, and it is used in dissolving particles of these metals from their ores. It forms many double and complex cyanides with the cyanides of other metals, such as $\text{NaAg}(\text{CN})_2$ or $\text{NaAu}(\text{CN})_4$; and solutions of such salts are used as electrolytes in many processes of metal plating.

Sodium cyanide is made from metallic sodium in two stages: Dry ammonia gas is passed over hot sodium with the formation of sodium amide, often called sodamide, NaNH_2 , a white solid:



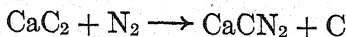
The resulting sodium amide is then heated with carbon:



As explained in the next paragraph, sodium cyanide can also be made by heating a mixture of calcium cyanamide, carbon, and salt.

Potassium cyanide, KCN , is very similar to sodium cyanide but is no longer of much importance.

Calcium cyanamide (CaCN_2). This compound is formed when nitrogen is passed over calcium carbide heated to about 1200° :

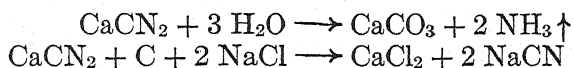


The compound is a derivative of *cyanamide* ($\text{CN} \cdot \text{NH}_2$ or H_2CN_2), with the two hydrogen atoms replaced by a calcium atom. The commercial product, known as *lime nitrogen*, contains about 60 per

cent of cyanamide, and the remaining 40 per cent consists chiefly of carbon and lime. This is ground and mixed with water (which slakes the lime) and in this form is sold as a fertilizer under the name *cyanamide*. Its value as a fertilizer lies in the fact that all its nitrogen is available as a plant food.

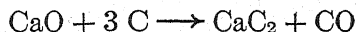
Calcium cyanamide has also been used in the commercial preparation of ammonia and of sodium cyanide. Ammonia is obtained

by treating the cyanamide with steam, while the cyanide results from the action of carbon and sodium chloride. The equations for the reactions are as follows :



The nitrogen used in the preparation of the cyanamide is obtained from liquid air (p. 140). By these reactions it is possible to convert the nitrogen of the air into important compounds of nitrogen.

Calcium carbide (CaC_2). This compound is produced on a very large scale, chiefly in places where abundant water power is available. It is made by heating a mixture of coke and lime in electric furnaces :



The pure carbide is a colorless, transparent, crystalline substance. It is insoluble in all solvents, but is readily decomposed by water. The commercial product is a dull-gray porous substance which contains many impurities. It is used in manufacturing cyanamide as a fertilizer, and for generating acetylene for its many uses. At high temperatures it is a powerful reducing agent.

Commercial production of calcium carbide. The general form of furnace used for making calcium carbide on a large scale is shown in Fig. 336. The sides and bottom of the furnace are built of brick, and large carbon electrodes A, A, A, A extend into the furnace. The furnace is nearly filled with a mixture of coke and lime B. The current is then connected and regulated

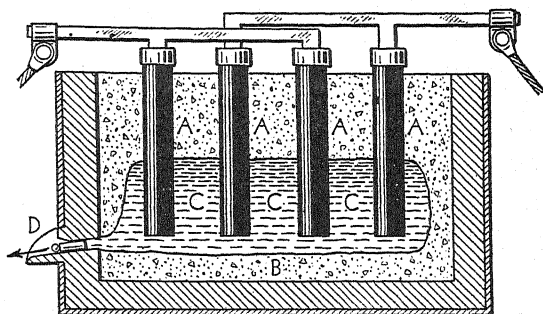


FIG. 336. A Furnace for the Production of Calcium Carbide

so as to secure a temperature of about 2000° . At this temperature the carbide gradually forms. As the temperature is above its melting point, the carbide separates in liquid form *C*, *C*, *C* and is drawn off at the outlet *D*. The process is continuous, the raw materials being added from time to time as the carbide is withdrawn. These furnaces are really large brick rooms.

Flame tests for the metals. The alkali and alkaline-earth metals are remarkable for the colors given to a Bunsen flame by small quantities of their volatile salts, especially by their chlorides. A clean platinum wire dipped into a solution of one of the chlorides and held in the flame (Fig. 337) at once shows the characteristic color

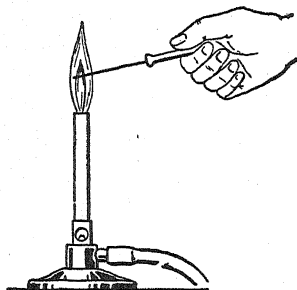


FIG. 337. *Method of Making a Flame Test*

Colors from Compounds of the Metals

METAL	COLOR OF FLAME
Lithium . .	deep red
Sodium . .	yellow
Potassium .	pale lilac
Rubidium .	crimson
Cesium . .	sky blue
Calcium . .	brick red
Strontium .	bright crimson
Barium . .	green

due to the metal. The heat dissociates the chloride into its ions, which emit light of characteristic wave lengths as they combine again. If more than one metal is present, each may be identified by viewing the colored flame with a spectroscope (p. 144). The nitrates of strontium and barium give these same colors when mixed with combustible material and set on fire. They are manufactured for use in red or green signal flares or fireworks.

Some insoluble compounds of the metals. Knowledge of what compounds of each metal are insoluble is a great help in devising ways of preparation (p. 552). In addition, many methods of analysis depend on the precipitation and isolation of very insoluble compounds.

Sodium forms practically no insoluble compounds. Lithium forms almost insoluble carbonate, phosphate, and fluoride. Potassium (as well as rubidium and cesium) forms the following compounds which are nearly insoluble in water and less so in alcohol: the perchlorate, KClO_4 ; the chloroplatinate, K_2PtCl_6 ; the potassium-sodium cobaltinitrite, $\text{K}_2\text{NaCo}(\text{NO}_2)_6$. Calcium is separated as the insoluble oxalate, CaC_2O_4 , and barium as the sulfate, BaSO_4 . Strontium has no compounds that give easy separations.

Compounds of sodium and potassium contrasted. With the close of this chapter the student may wonder why so many more compounds of sodium have been described than of potassium. There are several reasons for this.

Potassium is more costly than sodium, and in most cases the sodium salt serves all the purposes of the potassium salt. When the latter is used, it is because it has distinct advantages.

Potassium salts are less soluble than sodium salts; they are therefore easier to crystallize free from impurities and are not deliquescent. They rarely have water of hydration. This fact saves costs in transportation and prevents efflorescence. The corresponding salts of the two metals have different physiological actions.

Questions

1. (a) Potassium carbonate was much more widely used in early times than was sodium carbonate. Why? (b) Since sodium chloride is very abundant in nearly all countries, why did it prove to be so difficult to manufacture sodium carbonate?

2. Common salt is likely to contain as impurities the chlorides of calcium, magnesium, and potassium. How could you prepare a pure sample from the crude salt?

3. Hydrochloric acid is a stronger acid than sulfuric acid. Under what conditions and for what reason will sulfuric acid transform sodium chloride into sodium sulfate?

4. Why should the salt $\text{Na}_2\text{S}_2\text{O}_3$ be called sodium thiosulfate, since it does not contain the sulfate radical?

5. Although an acid salt, a solution of disodium phosphate has a slightly alkaline reaction. Why?

6. Are the salts of potassium or those of sodium the more frequently used? Name three considerations that determine the choice.

7. Why should ammonium sulfate be one of the cheapest of ammonium salts?

8. Metallic calcium reacts readily with water. Would this prevent its use in alloys?

9. If strontium and barium were as abundant as calcium, can you suggest any present uses of calcium that would be replaced by compounds of these two elements?

10. Men have been asphyxiated while working both at the top and at the bottom of limekilns. Why should this be?

11. Barium sulfate is but slowly changed by a solution of sodium carbonate, while in a *fusion* of that salt the change into barium carbonate is very rapid. Why?

Problems

1. In making 100 kg of hyposulfite of soda, what weight of sodium sulfite (anhydrous) is required?
2. What raw materials and what weight of each would be required to prepare 100 kg of sodium carbonate by the Solvay process?
3. One hundred kilograms of a soluble carbonate was required in a reaction to furnish CO_3 ions. If potassium carbonate (anhydrous) costs twice as much as crystallized sodium carbonate, which would be the cheaper?
4. A glass company uses 5 tons of anhydrous sodium sulfate daily. If the yield is 90 per cent of the theoretical, (a) what would be the daily consumption of sodium chloride necessary to produce this sulfate? (b) what would be the yield of hydrogen chloride? (c) If the latter were to be dissolved in water to make a solution of density 1.18 and containing 36 per cent HCl , what would be the volume of the solution?
5. A limekiln uses 50 tons of limestone daily. Assume the molecular weight of calcium carbonate to be 100, and the material to be 90 per cent pure. (a) Without use of atomic weights, calculate the volume of carbon dioxide, under standard conditions, that will be evolved. (b) What weight of Dry Ice will this make if we assume no loss of the carbon dioxide?
6. A firm has available daily 1000 kg of pyrite (FeS_2) for the manufacture of calcium sulfite to be used in a paper mill. From this source of sulfur what weight of calcium sulfite can be furnished daily?

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- RICHARDSON. "Calcium Chloride for Snow Removal," *Journal of Chemical Education*, Vol. VII, pp. 441-442.
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CHAPTER 33

Some Less Active Metals and Their Compounds

ELEMENT AND SYMBOL	ATOMIC WEIGHT	ATOMIC NUMBER	DENSITY	MELTING POINT	ELECTRONS IN SHELLS
Beryllium (Be)	9.02	4	1.84	1280°	2:2
Magnesium (Mg) . . .	24.32	12	1.74	651°	2:8:2
Zinc (Zn)	65.38	30	7.14	419.43°	2:8:18:2
Cadmium (Cd)	112.41	48	8.6	320.9°	2:8:18:18:2
Aluminum (Al)	26.97	13	2.702	660°	2:8:3

The group of metals. In this chapter we shall study the first two metals in Group II of the periodic table, and the two that follow these in family *B*. We shall also include aluminum, the second element in Group III. It resembles beryllium and magnesium in both physical and many chemical characteristics, although it is trivalent and its salts differ in formula from those of the four other metals under consideration. The metals that follow aluminum in both family *A* and family *B* are all rare elements, and little need be said about them. Mercury, following cadmium in Group II, will be studied along with silver and copper for reasons that will appear later.

Historical. The existence of all these metals in the form of oxides or other compounds has been recognized for a long time. In Europe zinc was the first one to be isolated as a distinct metal by Marggraf in 1746, and cadmium was discovered as an impurity in zinc by Stromeyer in 1817. Marggraf also first definitely recognized the difference between soda and potassa, and between alumina, magnesia, and calcia. Joseph Black (Scottish) independently demonstrated the difference between MgO and CaO a few years earlier.

Metallic zinc was obtained by distilling the oxide with carbon, and cadmium was separated from zinc by repeated distillation. Very small quantities — really specimens — of the other metals were obtained by heating their anhydrous chlorides or fluorides with metallic potassium or sodium; and it was by this reaction that the early commercial aluminum was made.

Ores of the metals. All the metals in this group are found in nature as silicates, and some of them as useful carbonates, sulfides,

or chlorides. The ore for each metal must be chosen from the most economically available mineral, and it happens that a different type of mineral is best suited for each.

Beryllium is prepared almost exclusively from *beryl*, which occurs along with feldspar and mica in hexagonal crystals often of great size. The chief deposits in the United States are in South Dakota, California, and Maine; but the mineral is nowhere abundant. It is a silicate of the formula $3 \text{BeO} \cdot \text{Al}_2\text{O}_3 \cdot 6 \text{SiO}_2$, and emerald (tinted green with compounds of chromium) and aquamarine (tinted light green or blue with compounds of iron) are gem varieties of beryl.

Magnesium is made from the chloride recovered from salt brines and sea water, or made from the natural carbonate. Aluminum is made from the mineral *bauxite*, which is a hydrated oxide, whose composition varies from $\text{Al}_2\text{O}_3 \cdot 2 \text{H}_2\text{O}$ to $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$.

Cadmium occurs associated with zinc, and the most useful ores of the two are the sulfide, ZnS (sphalerite), and the double oxide, $\text{ZnO} \cdot \text{Fe}_2\text{O}_3$ (franklinite). In the United States the former is found most extensively in the "tristate" district, which includes portions of Oklahoma, Kansas, and Missouri; the latter, in New Jersey and bordering states. Other useful ores are the carbonate and silicate.

Metallurgy — general. In the metallurgy of these metals two entirely different plans are followed: reduction of the oxides by carbon, and electrolysis.

Reduction by carbon. Zinc, cadmium, and in a modified sense beryllium are obtained by reduction of their oxides by carbon.

The sulfide of zinc (containing cadmium) is first concentrated by flotation (p. 542) and then heated with free access of air (roasted) to convert the sulfide into oxide. The oxide is mixed with coal (carbon) and heated in earthenware retorts. The carbon reduces the oxide, and the zinc distills (boiling point 907°) and is condensed in suitable receivers. While the receivers are still cold, the zinc condenses as a powder called *zinc dust*, or *blue powder*, which consists of metallic zinc with about 5 per cent zinc oxide. When the receiver has become hot, the zinc collects in liquid form. Cadmium boils at a lower temperature than zinc (767°) and collects in the earlier portions of the zinc. It can be recovered by fractional distillation or by chemical separation from the zinc. Unrefined zinc is called *spelter* zinc.

An alloy of beryllium with copper can be produced by carbon reduction of a mixture of the oxides of beryllium and copper, but it is necessary to add a powerful *oxidizing* agent, whose oxidation of carbon liberates an excess of chemical energy to bring about the reduction of the beryllium oxide. Much beryllium-copper alloy is produced in this way.

Magnesium oxide can be reduced by carbon, but only at a very high temperature, at which the magnesium vapor produced is extremely active.

This fact introduces many problems of condensation, and the process is not as yet a commercial one.

Electrolytic reduction from water solutions. About one fourth of the zinc produced in the United States is obtained by leaching the ores with sulfuric acid, by which means the zinc passes into solution as zinc sulfate, ZnSO_4 . This solution is then electrolyzed, and the zinc is deposited on a cathode of pure zinc, as in the process of electroplating. As the zinc is deposited, the solution becomes more and more acid, and is finally used to leach a new portion of ore.

Electrolytic reduction from fused electrolytes. This important process began on an industrial scale with the electrolytic production of sodium and of aluminum, and an account of its development will throw much light on the production of all similar metals.

Historical. Aluminum was first prepared in relatively pure form by the German chemist Wöhler over a hundred years ago (1827), by heating anhydrous aluminum chloride with potassium. But the samples prepared in this way were for years a mere chemical curiosity for museum shelves, owing to the expense of preparation. Specimens could be procured at a cost of about \$160 a pound. In 1854 the French chemist Deville substituted the metal sodium for the more expensive potassium, and within a few years the price dropped to \$20 a pound. Further progress seemed then to depend upon cheaper sodium. Electrolytic sodium, developed by the American Castner, went a long way toward meeting this requirement; and for a brief period aluminum could be purchased for about \$5 a pound, but by 1883 only 83 pounds had been produced.

Toward the end of his course as a student in Oberlin College, young Charles Hall (Fig. 338) determined to solve the problem of the production of aluminum and soon became convinced that an electrolytic process was the only hope. Electrolysis of aqueous solutions was known to be a failure. Electrolysis of melted cryolite, a mineral of the formula Na_3AlF_6 , found in Greenland, had been equally unsuccessful. Hall reasoned that if he could find some melted material that would dissolve aluminum oxide, possibly the oxide would prove to be an electrolyte in such a solution. Among other things he tried the mineral cryolite, and found that it melted easily and readily dissolved aluminum oxide. He rigged up a number of makeshift batteries and a small furnace in a woodshed, melted the cryolite in the furnace, added aluminum oxide, and applied the current; and one morning some months after graduation he rushed over to his professor of chemistry, holding in his hands a few globules of the electrolytic metal. This was in 1886. A few months later a young Frenchman, P. L. T. Heroult, devised exactly this same process, but the Hall patents were granted priority. The large-scale process of today is essentially the same as the one devised by Hall in his woodshed.

The Hall electrolytic process for aluminum. A great industry for the metallurgy of aluminum developed rapidly following the discovery of Hall, not much over fifty years ago (Fig. 339). Fused cryolite, Na_3AlF_6 , or an artificial mixture of fluorides of the alkali and alkaline-earth metals constitutes the solvent in the electrolytic cell, and aluminum oxide is the electrolyte. The oxide is obtained from the mineral *bauxite*,



FIG. 338. *Charles Martin Hall*
(1863–1914)

View of an aluminum statue of Hall
at Oberlin College

which is a mixture of the hydrated oxides of aluminum $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ and $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$, together with similar compounds of iron. The purification of the oxide is one of the chief items of cost in the process. The bauxite produced in the United States comes chiefly from Arkansas and Georgia; but we import about two thirds of our ore from abroad, principally from South America. Of course aluminum oxide *could* be obtained from common clay, but probably this will not be done while bauxite is available.

Electrolytic production of beryllium and magnesium. The electrolytic production of beryllium and of magnesium follows closely the pattern set by that of aluminum. Be-

ryllium melts at a very high temperature; this necessitates the use of an electrolyte which is a mixture of high-melting fluorides of beryllium and of alkali and alkaline earths, such as BaF_2 . As the beryllium is deposited at the cathode, fluorine is set free at the anode. Magnesium melts at a much lower temperature, and the electrolyte used is essentially anhydrous magnesium chloride, MgCl_2 . Magnesium is liberated at the cathode, floats on the electrolyte, and is skimmed off. Chlorine is evolved at the anode. In both these processes the melted salts themselves constitute the electrolyte, while with aluminum it is the added and dissolved oxide.

Chemical activity of the metals. All these metals are above hydrogen in the electromotive series, and we should expect them to

be very active. Beryllium is the least active toward water at ordinary temperatures. It will be noticed that its melting point is very high for so light a metal, which means that in the solid state the inter-atomic forces are very strong, and chemical activity weak. Cadmium and zinc are the next least active metals, and magnesium and aluminum the most active.

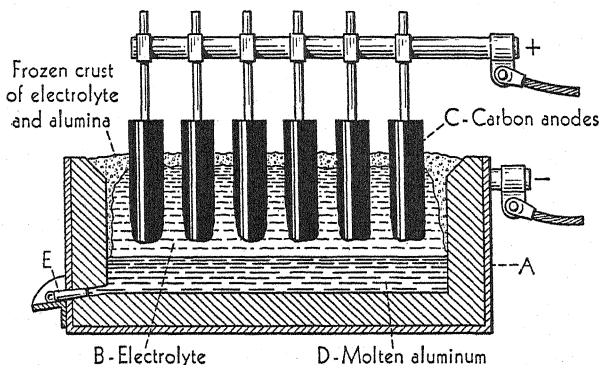


FIG. 339. *The Electrolytic Production of Aluminum*

The process is carried out in carbon-lined iron boxes, into which project carbon electrodes *C*. The apparatus is connected with an electric generator in such a way that the carbon-lined boxes serve as the cathode and the carbon rods *C* as the anodes. Each box is partially filled with cryolite (or a similar artificial material), and the current is turned on, generating sufficient heat to melt the cryolite. Aluminum oxide is then added and dissolves in the liquid cryolite as an electrolyte. Upon electrolysis it yields aluminum and oxygen. The temperature is maintained above the melting point of aluminum, and the liquid metal, being heavier than cryolite, sinks to the bottom of the vessel, from which it is tapped off from time to time through the taphole *E*. Part of the oxygen escapes as gas, and part of it combines with the carbon of the anodes. As the oxide is electrolyzed, more is added, so that the process is continuous

These two metals, as well as zinc, fail to act readily on water because a thin invisible film of oxide (with zinc a basic carbonate) forms on their surface as an impervious protection. All the metals evolve hydrogen readily from those acids which do not act as oxidizing agents, such as hydrochloric acid; even as weak an acid as acetic acid corrodes aluminum more rapidly than nitric acid. It is because of the protection of this film of oxide that such active metals as magnesium and aluminum can have such a wide use. Salt solutions corrode all these metals rather rapidly, and alkalis attack beryllium, aluminum, and zinc.

Uses of the heavier metals — zinc and cadmium. The densities of zinc and cadmium are not so very different from that of iron. These two conform more nearly to the usual idea of a metal, but

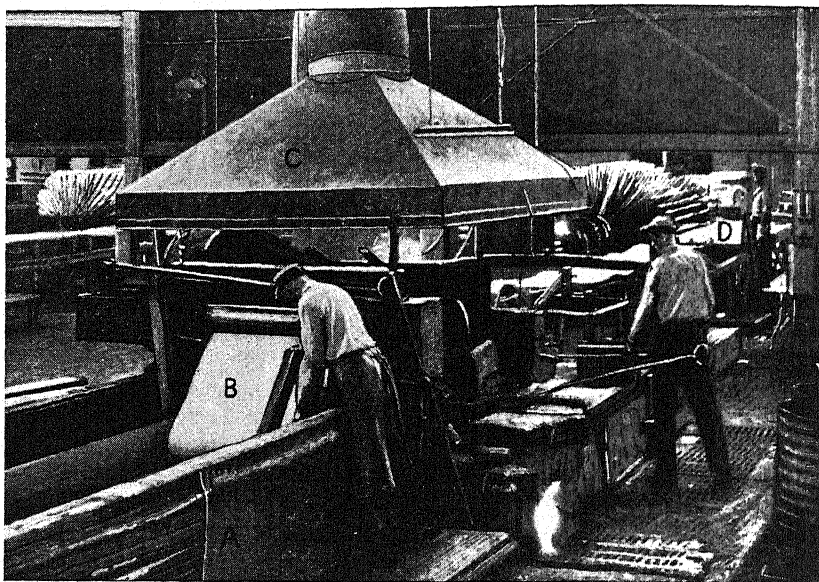


FIG. 340. *Galvanizing Sheet Iron*

The sheets of iron *B* are first cleaned by passing them through a vat *A* of dilute acid. They are then passed through a kettle of molten zinc, placed under the hood *C*, which carries away the poisonous fumes. The sheets are then passed between rollers, thus forming the finished product *D*

neither of them has the strength required for most uses of the heavier metals. They are chiefly protective and alloy metals.

Some zinc is used in nearly pure condition as linings for sinks or water containers, or for the anodes of dry cells. Some is used in the extraction of silver from lead (see Parkes process). Approximately half the zinc produced is used as a protective covering on iron to protect the iron from rusting. This covering is applied in several ways. Usually sheets of iron are dipped in a bath of melted zinc and then rolled smooth between rollers (*galvanized iron*) (Fig. 340). Sometimes the iron is electroplated by drawing iron objects, such as iron pipes, which serve as the cathode, through a bath of zinc salts (cold galvanizing). Some iron objects, such as steam boilers, are covered with zinc by use of a spray gun blowing a spray of melted metal. Small objects of iron are often rotated in a barrel containing zinc dust and become covered with an even layer of zinc (*sherardized iron*). The third major use of zinc is as an alloy metal. Brass is an alloy of copper and zinc; many bronzes, bearing metals, and ornamental metals of various kinds contain zinc as a component.

Cadmium has more limited uses because it cannot be produced in large tonnages. Like zinc it can be plated or sprayed on iron, and objects so protected are more pleasing in appearance and more durable than zinc-covered ones. Small automobile parts are usually cadmium-covered. In small percentages cadmium adds very desirable qualities to bearing metals, and alloys containing small percentages of cadmium and of silver are in wide use for automobile bearings. A number of low-melting alloys contain larger percentages of cadmium.

It may seem strange that iron can be protected from rust by a covering of a metal *above* it in the electromotive series. The explanation is found in the nature of the rust on iron and on zinc. Iron rust tends to break down into a porous condition, which permits the penetration of air and water deeper and deeper into the metal. The covering of "rust" on zinc is not porous, and acts as an airtight and watertight protective covering.

Uses of the lighter metals. We have been living in a world of heavy things — heavy utensils, heavy machinery, heavy construction in buildings, heavy bridges, heavy railway coaches, and heavy automobile bodies. Our construction metals have averaged between 7.5 and 8.5 in density. We are moving into an age which demands that all these things shall be lighter in weight, with the aircraft as the shining example. So wherever it is possible, we are turning to aluminum, one third as heavy as iron, and to magnesium, one fourth as heavy. These metals or their alloys can be brought into forms that are as hard, strong, malleable, and ductile as steel and as resistant to corrosion, and that are as good electrical conductors as copper or better than copper, weight for weight. So we are witnessing many changes. The annual production of aluminum in the United States is about 150,000 tons and that of magnesium about 2400 tons, though both figures depend on industrial conditions. The price of aluminum has been about 20 cents a pound, and that of magnesium approximately 30 cents.

Aluminum and its uses. Aluminum is a silvery metal whose luster soon dulls because of superficial oxidation. Below about 150° it is ductile and malleable and has high tensile strength. For a given cross section of wire it is not as good an electrical conductor as copper; but weight for weight it is much better, and this makes it adapted to long-distance power lines. Aluminum has long been a familiar metal in the form of kitchen utensils, small containers, foil, and powder in silvery paints. Slowly but surely it has become a great building material for roofing, cornices, window frames, ornamental

fittings, and even for furniture. A modern office building may contain as much as 100,000 lb of the metal. Gas tanks, bodies of railway coaches, trucks, automobiles, and aircraft are made largely of aluminum.

For many of these purposes, as well as for many more specialized ones, alloys of aluminum are better than the pure metal; and many of these alloys contain the newer metal magnesium. For example, the very strong alloy *Duralumin* contains 4 per cent copper, 0.5 per cent magnesium, and 6 per cent manganese. It has a tensile strength equal to that of medium steel and double that of furnace aluminum. *Magnalium* is an alloy of aluminum with from 10 to 20 per cent of magnesium. An alloy is more likely to suffer corrosion by liquids than is a pure metal because of electromotive forces at the juncture of crystal particles. For this reason sheets of *Duralumin* and of some other alloys are sometimes coated with pure aluminum, and this combination has the trade name *Alclad*.

Magnesium and its uses. Like aluminum, magnesium is a silvery metal that tarnishes to a dull-gray surface through oxidation. It is about two thirds as heavy as aluminum. It burns with a brilliant white flame, and the powdered metal mixed with an oxidizing agent is used in fireworks and signal flares. This light is rich in light waves that affect photographic plates, and the metal was formerly used in flashlight powders; but for this use it has been replaced by very thin aluminum foil (Fig. 6). Magnesium is used in purifying other metals (see below); otherwise it is used almost entirely as an alloy metal. In this country the development of these alloys began about 1920, and the best-known ones are called *Dowmetals*. They contain from 85 to 99 per cent of magnesium, and are light, strong, easily machined, and weather-resisting. They can be cast, forged, rolled into plates, drawn into rods, or pressed into tubes; and they are especially useful in replacing copper or iron where lightness is important, as in the body structure of aircraft, in home appliances, and in machine parts such as the pistons in gas engines.

Beryllium and its uses. Beryllium is the latest addition to the list of light industrial metals, the lightest of those in this group, and the hardest to get. As yet it has practically no uses as a pure metal but is used wholly in alloys. It is a hard, high-melting metal and adds hardness and strength to other metals, particularly to copper. The chief alloy of beryllium is a copper alloy containing about 2.25 per cent of beryllium. This alloy is golden in color, has great tensile strength, and can be heat-treated to produce remarkable springs that show no "fatigue" with use. A similar alloy with nickel makes a high-melting smooth-bearing metal, especially adapted

to the demands of aircraft engines. In small percentages beryllium improves many varieties of rustless steel that contain nickel, cobalt, or chromium.

The light metals as gas-absorbers and metal-purifiers. In making high-vacuum tubes, such as radio, X-ray, or thermionic tubes, one of the great problems has been to remove the last traces of the original atmospheric gases, chiefly oxygen, nitrogen, and water vapor. To accomplish this removal, a small pellet of one of the very active metals is placed in the tube before it is evacuated and sealed; and after the tube is sealed, the pellet is heated. Nearly any one of the alkali or alkaline-earth metals, as well as magnesium or aluminum, will combine energetically with these residual gases to form solid products and improve the vacuum.

In a similar way the alkaline-earth metals or magnesium or aluminum are sometimes melted with heavy metals, such as iron or nickel, as they are poured. The active metals take away any trace of oxygen, nitrogen, or sulfur remaining in the less active metal, and the products formed pass off to the surface of the metal, leaving it free of blowholes or particles of oxides. Metals used for this purpose are called *scavengers*, or purifiers, and this is one of the large uses of both aluminum (for iron) and magnesium (for nickel).

Goldschmidt reduction and welding process. Aluminum has a great affinity for oxygen and is able to reduce the oxides of many metals that are difficult to reduce by other means, such as those of manganese or chromium (p. 544). A great deal of heat is set free in such reductions, and this fact was turned to account in the process of welding iron by the German chemist Goldschmidt. The iron joint to be welded is cleaned and heated with a gasoline torch. A mixture of iron oxide, Fe_2O_3 , and finely divided aluminum is prepared, often with the addition of an oxidizing agent, such as barium peroxide, BaO_2 , to increase further the heat. This mixture, called *Thermit*, is placed in a funnel-shaped clay crucible immediately over the joint (*B*, Fig. 341), and the reduction of the iron oxide by the aluminum is started by igniting a primer wire of magnesium. The white-hot iron is then allowed to flow into a form surrounding the joint to make the weld (*A*, Fig. 341). Electrical welding is largely replacing this Thermit process except in special cases.

The oxides of the metals. The oxides of the five metals we are considering are all white solids, except cadmium oxide, which is brown; and the only one found in nature to any extent is aluminum oxide. The oxides of magnesium, aluminum, and zinc are the ones of industrial importance.

Zinc oxide, ZnO , or *zinc white*, is made industrially in two general ways: Crude spelter zinc or scrap zinc is burned in air, and the oxide produced is collected. Minerals containing zinc in the form of oxidized compounds (franklinite, $\text{ZnO} \cdot \text{Fe}_2\text{O}_3$, or smithsonite, ZnCO_3) are heated in a retort with carbon or in a current of carbon monoxide, CO , and the zinc vapors are burned as they issue from the retort. The oxide is filtered from the excess air by cloth filters. Most American oxide is made by the latter process. The oxide is used chiefly as a filler in white rubber goods and as a white paint pigment. Smaller quantities are used in making glasses and glazes and in oilcloths. Like all zinc compounds, zinc oxide is mildly poisonous, and it has long been used in antiseptic ointments.

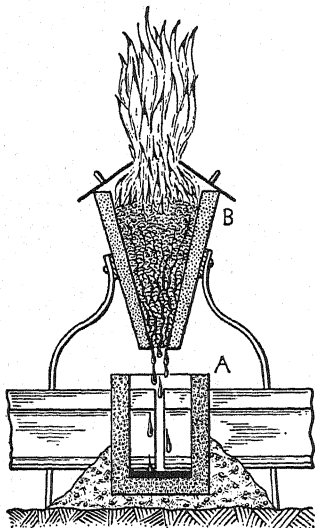
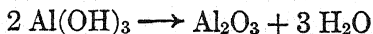


FIG. 341. *Welding Car Rails with Thermit*

Magnesium oxide, MgO , called *magnesia*, is made by heating magnesium carbonate (the mineral magnesite), which is more easily decomposed than the similar calcium carbonate. If not heated at too high a temperature, it is a very light, fluffy powder. In this form it will slowly combine with water to form the hydroxide, but more slowly than lime and with the production of less heat. It is used in making floor cements, stucco, and cement building materials. Heated above about 1400° , the oxide contracts, increases in density, become much less active, and melts only at a very high temperature (2800°). This form of the oxide is used in the manufacture of fire-brick, as a lining for furnaces, and for other fire-resisting purposes.

Aluminum oxide, Al_2O_3 , is found in nature as the relatively pure colorless mineral *corundum*, and as *emery* when colored brown or black with iron oxide. In transparent crystals, tinted with oxides of various metals, such as chromium, titanium, cobalt, iron, or manganese, it is a precious gem stone, and includes ruby (red), sapphire (blue), Oriental topaz (yellow), and Oriental amethyst (violet). All these varieties are almost as hard as diamond, and the cheaper ones, corundum and emery, are used as abrasives. The pure oxide is obtained as a white powder by heating the hydroxide:



By heating the impure natural hydroxide (bauxite) an abrasive is produced that is superior to the natural oxide and is sold under various trade names, such as *Alundum* and *Aloxite*. Some forms of firebrick, and crucibles and tubes for laboratory use, are made from these materials.

Artificial gems. Aluminum oxide can be melted in oxyhydrogen furnaces, and obtained in crystalline form. The pure colorless gem so produced is called white sapphire; by adding the requisite metallic oxide almost any desired color can be given the gem stone. The rubies and sapphires so produced are identical in almost every respect with the natural stones and are artificial gems, not imitation ones.

Abrasives. Abrasives are hard substances easily powdered to grains of various sizes, and used for grinding and polishing purposes. Sandpaper and emery paper are familiar examples. Many machine parts, such as the valves of an automobile engine, must be accurately fitted by grinding; and the demand for harder and harder abrasives increases with the hardness of materials used in machines. Artificial abrasives have largely displaced the natural ones, and the artificial oxides of aluminum, together with hard carbides, such as Carborundum (p. 422), are examples of the newer abrasives.

The hydroxides. The hydroxides of magnesium, zinc, and aluminum are all white, nearly insoluble solids which are thrown down from soluble salts of the metals by ammonium hydroxide or sodium hydroxide as flocculent precipitates. Each differs from the other in interesting chemical properties.

Hydroxides of magnesium and zinc. Magnesium hydroxide, $\text{Mg}(\text{OH})_2$, is found in nature as the mineral *brucite*; an enormous deposit of 96 per cent purity occurs in Nevada. It is used chiefly as a source of magnesium oxide for furnace linings. The precipitated hydroxide, suspended in water (milk of magnesia), is used as a medicine to overcome too much stomach acidity. Zinc hydroxide, $\text{Zn}(\text{OH})_2$, has no important uses.

Aluminum hydroxide, $\text{Al}(\text{OH})_3$. As we have seen, this hydroxide, in a partially dehydrated form, constitutes the mineral bauxite and is the chief ore of aluminum. It is a very weak base, and its salts are extensively hydrolyzed in solution unless they are salts of the strongest acids. It forms a colloidal jelly that has high adsorptive properties; when dried, this jelly changes into a porous oxide that is much used as a catalyst in many reactions. The production of colloidal hydroxide in solutions of various kinds is important in water purification and in the art of dyeing.

Action of excess of alkali on the hydroxides. All these hydroxides are precipitated by a limited quantity of alkalies or ammonium hydroxide, and zinc and aluminum dissolve in excess of one or the other of these reagents but for different reasons.

Magnesium hydroxide does not dissolve in excess of alkalies, but it fails to form at all if ammonium salts are present in the original solution. This is because it is the most soluble of these three nearly insoluble hydroxides (as well as of other similar hydroxides, such as $\text{Fe}(\text{OH})_2$). To cause precipitation of $\text{Mg}(\text{OH})_2$ there must be a sufficient concentration of OH^- ions to cause the solubility product of magnesium hydroxide to be exceeded. The solubility product is expressed in the equation

$$[\text{Mg}^{++}] \times [\text{OH}^-]^2 = K \text{ (see page 342)}$$

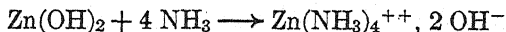
Ammonium hydroxide alone and in small quantities will precipitate magnesium hydroxide because it gives enough ions to exceed the solubility product of the hydroxide. But ammonium hydroxide is a very weak base, and, if there are freely ionized ammonium salts present, the excess of ammonium ions, NH_4^+ , combine with the OH^- ions of the added alkali to form nonionized NH_4OH to such an extent that there are no longer enough OH^- ions to cause the solubility product of magnesium hydroxide to be exceeded. No precipitation takes place.

Zinc hydroxide dissolves in excess either of sodium hydroxide or of ammonium hydroxide. It is an amphoteric hydroxide, and its solution in sodium hydroxide is usually represented by the equation

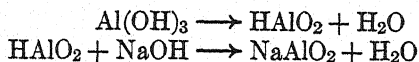


The crystals that form from the solution have the formula $\text{Zn}(\text{ONa})_2 \cdot 2 \text{H}_2\text{O}$, and it is probable that the compound should be represented by the formula 2Na^+ , $\text{Zn}(\text{OH})_4^{--}$. Zinc has formed a complex *anion* $\text{Zn}(\text{OH})_4^{--}$.

In excess of aqueous ammonia (NH_3 is present as well as NH_4^+ and OH^-) zinc hydroxide dissolves because the zinc ions form a complex *cation*:



Aluminum hydroxide does not form complex ions with ammonia, and is precipitated by ammonium hydroxide because it is very insoluble. Like zinc hydroxide, it dissolves in excess of sodium hydroxide:



In the solid state the compound always contains water of crystallization, so that the more likely formula is Na^+ , $\text{Al}(\text{OH})_4^-$.

Like aluminum hydroxide, beryllium hydroxide is soluble in alkalies but not in ammonium hydroxide.

Use of aluminum hydroxide. Aluminum hydroxide adsorbs many soluble coloring substances, forming insoluble products, and this property leads to its wide use in the dyeing industry. Many dyes will not adhere to natural fibers, such as cotton; that is, they will not dye fast. Cloth woven from such fibers may often be dyed in the following way: The cloth is first soaked in a solution of an aluminum salt, such as the acetate, which readily undergoes hydrolysis. It is then exposed to the action of steam, whereby the aluminum salt is completely hydrolyzed, so that the resulting aluminum hydroxide is thus thoroughly incorporated in the fiber. If the cloth is now dipped into a solution of the dye, the aluminum hydroxide fastens, or fixes, the color substance upon the fiber by mutual precipitation or by selective adsorption. A substance, such as aluminum hydroxide, which serves this purpose is known as a *mordant*, which means "biting," since it bites, or holds fast, the dye. The compounds which act well as mordants may be precipitated in solutions containing various dyes, and the precipitate will be highly colored, though not always of the same color as the dye. Colored precipitates of this kind are called *lakes*.

The carbonates. Of this group of metals, magnesium is the only one whose carbonate needs special attention. Zinc carbonate (the mineral smithsonite) is of some importance as an ore; aluminum hydroxide is too feeble a base to form a carbonate.

Magnesium carbonate, MgCO_3 , occurs abundantly in nature as the mineral magnesite and as the double carbonate $\text{CaCO}_3 \cdot \text{MgCO}_3$ (dolomite). These minerals are the chief source in the preparation of magnesium compounds, and furnish the oxide widely used for furnace linings and heat insulation. Dolomite is a very hard rock and is used for furnace linings, road ballast, and building stone.

When a soluble carbonate is added to a solution of magnesium salt, the white carbonate precipitate is not the normal carbonate but a basic salt of the approximate formula $3 \text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 3 \text{H}_2\text{O}$. It is called *magnesia alba* and is the basis of many cosmetics and soft polishing powders.

The chlorides. The chlorides of this group are all very soluble, colorless salts and are all hydrated when crystallized from solution. If these hydrates are heated to drive off the water of hydration, the chloride loses hydrogen chloride to form the oxide or a basic salt:



Magnesium chloride ($\text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$). Magnesium chloride is found abundantly in sea water, in salt brines, and salt deposits. In the latter case it often occurs as the crystallized double chloride $\text{KCl} \cdot \text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$ (carnallite); and when potassium chloride

is recovered from this salt, magnesium chloride becomes a by-product. From these natural sources (or by preparation from magnesite), magnesium chloride has become the compound from which all magnesium is prepared. Mixed with calcium chloride it is used to lay dust (p. 582). A floor plaster of magnesium oxide with a filler of fiber (wood or asbestos) moistened with magnesium chloride sets to a hard floor covering or cement consisting of oxy-chloride, $3 \text{MgO} \cdot \text{MgCl}_2 \cdot 10 \text{H}_2\text{O}$. It is much improved in quality by the addition of 10 per cent of finely divided metallic copper.

Zinc chloride (ZnCl_2). The normal chloride and the basic chloride, $\text{Zn}(\text{OH})\text{Cl}$, result from the evaporation of solutions of zinc in hydrochloric acid. The largest use of these compounds is as a flux in soldering and as a wood preservative; for, like zinc compounds in general, they are poisonous to bacteria.

Aluminum chloride ($\text{AlCl}_3 \cdot 6 \text{H}_2\text{O}$). This salt is very soluble in water and difficult to crystallize. The anhydrous salt is an easily vaporized solid and can be made by heating the metal in a current of chlorine or of gaseous hydrogen chloride and condensing the resulting vapor. It has many uses in organic syntheses and as a catalyst, particularly in "cracking" higher petroleum oils.

The sulfates. The sulfates of this group are all colorless, well-crystallized, hydrated salts of average solubility.

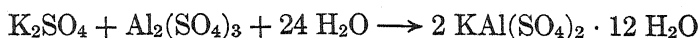
Magnesium sulfate. This salt occurs in many salt deposits, sometimes as the monohydrate $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ (kieserite), often as the hydrate $\text{MgSO}_4 \cdot 7 \text{H}_2\text{O}$, called *Epsom salt*, and as a constituent of various double salts. Epsom salt can be refined from the natural sulfate or made from the carbonate or chloride. It has long been used in medicine and has industrial uses in stiffening and dyeing cotton cloth and in tanning leather.

Zinc sulfate ($\text{ZnSO}_4 \cdot 7 \text{H}_2\text{O}$). This salt, called *white vitriol*, can be made by the action of dilute sulfuric acid on zinc, but for industrial uses it is made by leaching oxidized zinc ores with the acid. It constitutes the electrolyte in the electrolytic metallurgy and refining of zinc, and great quantities are used in the manufacture of the pigment lithopone (p. 585). It has minor uses in medicine and in the dyeing of cloth.

Aluminum sulfate ($\text{Al}_2(\text{SO}_4)_3$). This compound is prepared commercially by the action of sulfuric acid on either bauxite or kaolin. The latter is a silicate of aluminum occurring abundantly in nature. The sulfate crystallizes from water in quite a variety of hydrates, the usual one having the composition expressed by the formula $\text{Al}_2(\text{SO}_4)_3 \cdot 18 \text{H}_2\text{O}$. It is the cheapest of the soluble salts of alumi-

num and is therefore the one most largely used when a salt of this metal is desired. Its principal uses are in the manufacture of alum and paper, in the purification of water, and as a mordant in dyeing.

Alums. Aluminum sulfate has the property of combining with the sulfates of the alkali metals to form compounds called *alums*. Thus, with potassium sulfate the reaction is expressed by the equation



The sulfates of some other trivalent metals form similar compounds with the alkali sulfates, and these compounds are also called alums, though they contain no aluminum. They all crystallize in octahedra and contain 12 molecules of water of hydration. The alums most frequently prepared are the following:

Potassium alum	$\text{KAl}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$
Ammonium alum	$\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$
Ammonium iron alum	$\text{NH}_4\text{Fe}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$
Potassium chrome alum	$\text{KCr}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$

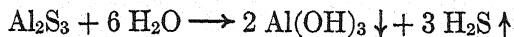
Since the alums crystallize so readily, it is easy to obtain them in pure condition. For this reason the aluminum alums have long been used in place of aluminum sulfate, which is difficult to purify. Improved processes have been devised for preparing the latter compound cheaply and in pure condition, so that now it is taking the place of alum for many commercial uses, such as the purification of water. In commerce the word *alum* is often used, at present, to denote aluminum sulfate. The alums are used in the manufacture of paper, in water purification, and as mordants in dyeing. Smaller quantities are used in baking powders and in certain foods, such as pickles, to make them more crisp.

The silicates. The silicates of this group of elements are of considerable importance. Beryl, the principal mineral of beryllium, is a complex silicate containing aluminum as well as beryllium. *Asbestos* and *talc* (*soapstone* or *French chalk*) are examples of silicates of magnesium. Soapstone is a valuable material for making sinks and table tops. Asbestos is soft and fibrous and is a nonconductor of heat and of electricity. Because of its fibrous character it can be spun and woven into fabrics. It is used for fireproof material in a great variety of forms, such as the fabric used for automobile brake-band linings, paper, board, and rope. It is also used as a covering for pipes, furnaces, and boilers, to diminish heat radiation; and it has many uses as an insulator in electrical devices. The chief source of asbestos is the province of Quebec, Canada. While the

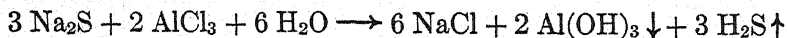
United States produces only about 2 per cent of the asbestos it uses, it nevertheless leads all other countries in the manufacture of asbestos products. In recent years *mineral*, or *rock*, *wool* has largely displaced asbestos as an insulator. This fibrous material is formed by directing a blast of high-pressure steam upon a thin stream of melted slag or rock. Willemite, zinc silicate, is an important ore of zinc in some localities.

The silicates of aluminum are widely and abundantly distributed and constitute by far the largest percentage of the igneous rocks (those formed by the cooling of the earth's original liquid mixture). Most important of these are the *feldspars*, known as *orthoclase* (KAlSi_3O_8), *albite* ($\text{NaAlSi}_3\text{O}_8$), and *microcline*, which has the same chemical composition as orthoclase but is different in crystalline structure. The gradual disintegration, or weathering, of these rocks through various agencies, such as the action of air, wind, and water, has resulted in the formation of the soft, plastic mineral known as *kaolin*, or *kaolinite* ($\text{Al}_2\text{Si}_2\text{O}_7 \cdot 2 \text{H}_2\text{O}$, often written $\text{Al}_2\text{O}_3 \cdot 2 \text{SiO}_2 \cdot 2 \text{H}_2\text{O}$), and other constituents of the soil. Large quantities of kaolin are sometimes found deposited in beds in fairly pure form. More often it has been carried away by running water and mixed with various other products resulting from the crushing and weathering of rocks, especially silica (sand) and compounds of iron, calcium, and magnesium, in this way forming the product known as *clay*. It is evident, therefore, that clay is extremely variable in composition, though the essential constituent appears to be kaolin. *Fuller's earth* is a name given to certain clays that possess the property of decolorizing and otherwise purifying fats and oils. Georgia and Florida furnish the largest supply, though it occurs in many other localities. *Bentonite* is a special type of clay mined in South Dakota; it has varied uses.

Hydrolysis of salts of aluminum. Although aluminum hydroxide forms fairly stable salts with strong acids, it is such a weak base that its salts with weak acids are readily hydrolyzed (p. 372). Thus, aluminum sulfide, which is formed by heating a mixture of aluminum and sulfur, is completely hydrolyzed upon the addition of water:

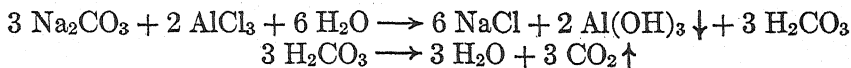


When a soluble sulfide, such as sodium or ammonium sulfide, is added to a solution of an aluminum salt, aluminum sulfide is not formed, but instead its hydrolysis products are obtained:



Similarly, the reaction of an aluminum salt and a soluble carbonate

produces aluminum hydroxide and carbonic acid, which decomposes to form carbon dioxide and water:



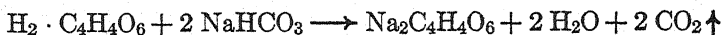
It is because of these reactions that an alum is used as a constituent of some baking powders.

Baking powders. Every baking powder contains three ingredients, the names and functions of which are as follows: (1) sodium bicarbonate to furnish the carbon dioxide; (2) some compound which, in the presence of water, reacts with the bicarbonate and slowly liberates carbon dioxide; (3) starch or flour, which serves to dilute the powder to the desired strength (not less than 12 per cent of available carbon dioxide) and at the same time prevents the powder from deteriorating by absorbing any moisture present. The compounds used for liberating the carbon dioxide are the following: (1) potassium acid tartrate, commonly known as cream of tartar; (2) tartaric acid; (3) calcium dihydrogen phosphate; (4) sodium aluminum sulfate (often designated as S.A.S.). Often certain mixtures of two of these compounds are used; thus, almost all cream of tartar baking powders also contain tartaric acid. The equations for the reactions that take place between sodium bicarbonate and each of the compounds given above are as follows:

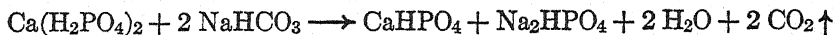
Potassium acid tartrate (cream of tartar):



Tartaric acid:



Calcium dihydrogen phosphate:



It is probable that other reactions than the one just given take place in the case of the phosphate powders, but this is the principal one.

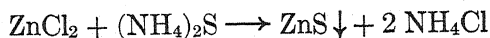
Sodium aluminum sulfate:



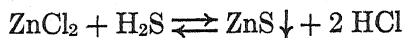
Sulfides. Magnesium sulfide (MgS), like aluminum sulfide, is formed by heating a mixture of the elements. This sulfide is a yellowish-gray solid and resembles calcium sulfide in its action toward water. The natural zinc sulfide (sphalerite, blende, or black-jack) varies, largely according to the impurities present, from a light-yellow, transparent, resinous solid to a black mass. The fact that, in the laboratory, zinc is the only one of the common metals

that forms a *white* insoluble sulfide is of importance in chemical analysis. Cadmium sulfide (CdS) occurs in nature as the mineral *greenockite*. In the laboratory it is prepared by passing hydrogen sulfide into a solution of a cadmium salt. Because this sulfide is bright yellow in color, it is used as a pigment and in making colored glass. It is the most important of the cadmium compounds.

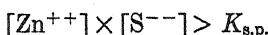
Formation of zinc sulfide by precipitation. Zinc sulfide is nearly insoluble in water and is formed as a precipitate when ammonium sulfide is added to a solution of a salt of zinc:



On the other hand, when hydrogen sulfide is passed into such a solution, the precipitation of the zinc sulfide soon ceases; for an equilibrium results, as expressed in the following equation:

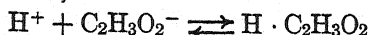


In accordance with the theory of precipitation (p. 342) this equilibrium results in the following way: While zinc sulfide is commonly said to be insoluble, because it is nearly so, it really has a very perceptible solubility. Before it can begin to precipitate, the concentration of the zinc ions and sulfide ions must be large enough to exceed the solubility product of the zinc sulfide, as expressed in the following equation:



There is an abundant concentration of the zinc ions supplied by the zinc salt; moreover, at the beginning of the reaction the concentration of the sulfur ions derived from the hydrogen sulfide is fairly large so that the solubility product ($K_{s.p.}$) of zinc sulfide is exceeded, and precipitation takes place. As the reaction proceeds, however, increasing quantities of hydrogen chloride are formed, and the hydrogen ions derived from this compound diminish the extent of the ionization of the hydrogen sulfide. The concentration of the sulfide ions, therefore, rapidly decreases until the solubility product of the zinc sulfide is no longer exceeded, and precipitation ceases.

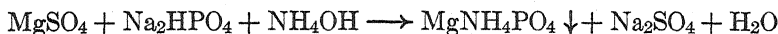
It is interesting to note, however, that if a normal salt of some weak acid, such as sodium acetate ($\text{NaC}_2\text{H}_3\text{O}_2$), is added to the solution of the zinc salt, and the hydrogen sulfide then passed in, the precipitation of the zinc sulfide continues to completion; for as fast as the hydrogen ions are formed in the reaction, they enter into an equilibrium with the anion of the weak acid, as shown in the following equation:



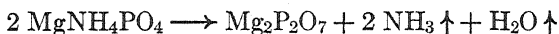
This keeps the concentration of the hydrogen ions too low to have any marked effect upon the concentration of the sulfur ions, so that precipita-

tion continues to completion. It may be added that the addition of sodium acetate to an acid solution is a device often employed when it is desired to reduce the concentration of the hydrogen ions to a minimum value and yet have the solution distinctly acid in reaction. This mixture of salt and acid is often called a *buffer solution*.

Other magnesium compounds. (1) *Magnesium nitride* (Mg_3N_2) is formed by the direct union of magnesium and nitrogen at high temperatures. It reacts with water to form magnesium hydroxide and ammonia. (2) *Magnesium citrate* (the magnesium salt of citric acid) is a common medicinal. (3) The *phosphates of magnesium* resemble those of calcium in their composition and general properties. When a solution of disodium phosphate is added to a solution of any magnesium compound containing ammonium hydroxide, magnesium ammonium phosphate is precipitated:

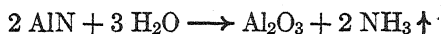


This crystallizes in the form of the hexahydrate, which is somewhat unstable. If filtered off and heated to redness, however, it is converted into magnesium pyrophosphate ($\text{Mg}_2\text{P}_2\text{O}_7$), which is perfectly stable:



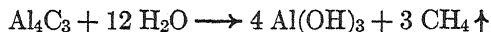
From the weight of the pyrophosphate it is possible to calculate the weight of magnesium present in the original solution. These reactions are used in the laboratory for the quantitative determination either of magnesium or of phosphoric acid.

Other aluminum compounds. 1. *Aluminum nitride* (AlN). This compound is prepared by direct union of aluminum and nitrogen at a high temperature. It derives its chief interest from the fact that when it is treated with steam, ammonia is formed:



The nitrogen used in preparing the nitride is obtained from the air. It is possible, therefore, through the intermediate formation of aluminum nitride, to convert the nitrogen from the air into ammonia.

2. *Aluminum carbide* (Al_4C_3). This compound was obtained by Moissan by heating aluminum oxide with carbon in an electric furnace. Its chief interest lies in the fact that it reacts with water to form methane:



Since methane constitutes nearly 90 per cent of natural gas, it has been suggested that the latter product may, in some cases at least, have resulted from the action of water upon the carbides formed when the crust of the earth was in a molten condition.

GALLIUM, INDIUM, AND THALLIUM

The other members of the aluminum family (gallium, indium, and thallium) are elements of rare occurrence in nature and were discovered by spectroscopic study of various minerals. They have brilliant and characteristic spectrum lines, and through these are known to be widely distributed in certain classes of minerals; with the exception of a few rare ores of thallium, however, they have never been found to an extent of more than about 0.1 per cent in any mineral. Like aluminum they are trivalent in their best-known compounds, but each of them forms at least one series of salts in which it is univalent or bivalent as well. Of these lower valence states, the univalent salts of thallium (thallous) are the best known. All three metals would find many uses if they were more available. At present thallium finds a limited use in certain alloys, but its chief use (as the sulfate Tl_2SO_4) is as a poison for ants and rats.

THE RARE EARTHS

History. In 1794 Gadolin discovered a new mineral, now called *gadolinite*, in the mines of Ytterby, near Stockholm, and found it to contain an oxide unlike any known at that time; this was named *yttria*. This same material has since been found in a great many minerals. Almost at once yttria was recognized as a complex substance, and from that time to the present day many chemists have been engaged in determining its composition. In all, seventeen very similar elements are now clearly recognized to be present in yttria, in addition to many other well-known ones of other character. Two of these, scandium and yttrium, fall into regular places in the periodic table. The other fifteen have consecutive atomic numbers and are known collectively as the *rare-earth metals*.

These elements caused a good deal of confusion because their properties are such that all belong in the same position in the periodic table. In the light of modern knowledge of atomic structure, this apparently anomalous situation finds a logical explanation.

Occurrence. Minerals containing these elements have been found in many different countries, including the United States. Some of these elements, for which delicate spectroscopic tests are known, are found to be widely distributed in many minerals, but in any appreciable quantities they are only of very local occurrence. As far as is known, no one of them ever occurs by itself, and a mineral which contains one is likely to contain most of them.

Table of the Rare-Earth Metals

ELEMENT	ATOMIC NUMBER	ATOMIC WEIGHT	ELEMENT	ATOMIC NUMBER	ATOMIC WEIGHT
Lanthanum . . .	57	138.92	Terbium . . .	65	159.2
Cerium	58	140.13	Dysprosium . .	66	162.46
Praseodymium .	59	140.92	Holmium . . .	67	163.5
Neodymium . .	60	144.27	Erbium	68	167.2
Illinium	61	(?)	Thulium . . .	69	169.4
Samarium . . .	62	150.43	Ytterbium . .	70	173.04
Europium . . .	63	152.0	Lutecium . . .	71	174.99
Gadolinium . .	64	156.9			

General characteristics. A number of reactions are known which separate these elements as a group more or less completely from all others, but no one of the rare earths, with the exception of cerium, can be separated from the others by a single precipitation of the usual kind. Separations are effected only by fractional recrystallizations or precipitations repeated hundreds and often thousands of times.

These elements are all trivalent, although a few of them are bivalent as well, and cerium is often quadrivalent. In general, they resemble aluminum, but their hydroxides are stronger bases, their salts are less hydrolyzed, and they form no alums. The salts of about half of these elements are colorless; those of neodymium are red, those of praseodymium green, those of samarium yellow, those of europium and terbium rose, and the ceric salts yellow or red.

Applications. A few practical applications have been found for some of these substances. By electrolyzing a mixture of a number of their compounds an alloy of the metals is obtained, known as *mixed metal* (*Misch-metal*). The heat of combustion of this alloy is greater than that of aluminum, and it is a more powerful reducing agent. It is therefore sometimes used in place of aluminum in the Goldschmidt process. An alloy of cerium with iron, known as *Auer metal*, produces brilliant sparks when drawn across a rough surface, and owing to this property it is used in the manufacture of gas-lighters and cigar-lighters. Some salts of cerium are used in medicine. Cerium oxide is a good catalytic agent in many reactions of oxidation, and it is also used in some enamels and in making glass for special purposes. Other applications are being sought, since at the present time large quantities of the mixed oxides are available.

Questions

1. (a) Outline the steps in the history of the development of aluminum production. (b) Describe in detail the modern electrolytic process.
2. Since aluminum is used for cooking vessels, it does not seem to be acted upon by water. Why, then, can it not be prepared by electrolysis of the aqueous solution of its salts?
3. (a) In addition to aluminum hydroxide, what other hydroxides are amphoteric? (b) How do you explain the fact that amphoteric hydroxides are always *very weak* acids and bases?
4. In addition to aluminum, what other elements or compounds have we found to combine directly with nitrogen?
5. (a) Why should aluminum sulfate displace alum for commercial purposes? (b) Would it serve in place of alum in a baking powder?
6. Make a comprehensive statement and comparison of the uses of aluminum, magnesium, and zinc, and explain the advantages of using these metals.
7. Since magnesium stands very high in the electrochemical series, why does it not decompose water rapidly?
8. (a) How could you distinguish between zinc hydroxide and magnesium hydroxide? (b) between Epsom salt and Glauber's salt?

Problems

1. Five hundred grams of feldspar (KAlSi_3O_8) was powdered and, by the addition of sulfuric acid, converted into crystallized alum. What weight of alum could be obtained theoretically?
2. What is the percentage of water of hydration in (a) crystallized aluminum sulfate? (b) potassium alum?
3. What volume of carbon dioxide (under standard conditions) could be obtained from a weight of calcium acid phosphate baking powder containing 100 g of calcium acid phosphate (together with an excess of sodium bicarbonate)?
4. Five hundred grams of aluminum was heated in an atmosphere of nitrogen to the completion of the reaction, and the product was then treated with hydrochloric acid. What weight of ammonium chloride was obtained?
5. What *relative* weights of sodium, zinc, cadmium, and aluminum will be required to yield 100 l of hydrogen by action on water or on acids? (Take sodium as unity for comparison.)
6. One thousand kilograms of an ore containing 5 per cent of zinc sulfide was leached with sulfuric acid, and the solution so obtained was then electrolyzed. What weight of zinc should be obtained?

7. A sample of dolomite weighing 1.3 g was dissolved in acid. After appropriate treatment the magnesium was all precipitated by disodium phosphate in the presence of ammonium hydroxide. The precipitate was heated to redness and 0.64 g of magnesium pyrophosphate was obtained. Calculate the percentage of magnesium carbonate in the original sample.

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- WADE. "Man-Made Gems," *Journal of Chemical Education*, Vol. VIII, pp. 1015-1026. Excellent article on the subject.
- WEEKS. *The Discovery of the Elements*. Read of the discovery of the elements discussed in this chapter.
- Consult the Minerals Yearbook for information concerning the source and production of each of the metals discussed in this chapter.

CHAPTER 34

The Ceramic Industries

The ceramic industries. There are a number of industries based upon the use of clay, sand, limestone, and feldspar in varying degrees of purity; and, in so far as they involve chemical transformations, they are closely allied. To a greater or less extent they depend upon the formation of silicates at high temperatures from the materials named, the bases of which are chiefly oxides of sodium, potassium, calcium, magnesium, aluminum, and iron. These industries are often called collectively the *ceramic industries*. They include those industries engaged in manufacturing various products from non-metallic, inorganic materials by processes that require high temperatures. They may be grouped roughly into three classes, according to whether they are most closely related to the manufacture of glass, cement, or clay products.

GLASS

Nature of glass. A glass is essentially a material which, on cooling from the state of a viscous liquid, has failed to crystallize and yet has become a rigid body; in other words, glass is an undercooled liquid. Pure silica, when fused and cooled, is an example of the simplest of glasses. The ordinary commercial varieties of glass are fused mixtures of silicates, together with excess of silica. When melted these ingredients all mix to form a homogeneous liquid; and when this is cooled, it gradually hardens to a glass.

Ingredients of ordinary glass. The ingredients used in making ordinary glass, such as window glass and bottles, are sand, limestone, dolomite, the carbonate and sulfate of sodium, and some compound of aluminum. When a mixture of these materials in the proper proportion is heated to fusion, the volatile anhydrides are driven out by the silica (p. 425), and the bases remain in the form of silicates. For glasses of fine quality pure materials must be used, while for cheap bottle glass ordinary sand, limestone (or dolomite), and soda ash will serve. When sodium sulfate is used, either alone or mixed with sodium carbonate, carbon is added to reduce the sulfate to sulfite, which is more easily decomposed by the silica.

Varieties of glass. By the proper selection and proportioning of the ingredients a great variety of glass can be made. Ordinary window glass is essentially a sodium-calcium-magnesium-aluminum glass.

Ordinary glass is perceptibly attacked by chemical reagents and even by water. For chemical glassware, such as beakers and flasks, it is necessary to use materials that will give a more resistant glass. In making such glass, a certain percentage of boric oxide is used along with the silica, so that the product is essentially a borosilicate of different metals, with large excess of silica. *Pyrex glass*, made to withstand shock and sudden changes of temperature as well as chemical action, is essentially a sodium-aluminum borosilicate containing an excess of silica. The addition of lead oxide makes a soft glass, but one which is very brilliant and has a high refractive index. Such a glass is suitable for some optical purposes and for the preparation of artificial diamonds and other imitation gems (*paste*).

Color of glass. The color of glass is usually due to the presence of colored metallic silicates. For example, ferrous silicate colors the glass green, while ferric silicate colors it yellow or brown. The green color can be changed to the less objectionable yellowish tint by the addition of manganese dioxide, which acts as an oxidizing agent, converting the ferrous into ferric compounds. In larger quantities manganese colors the glass violet. Cobalt compounds form deep-blue silicates, and many other metals produce characteristic colors. Sometimes the metals themselves are added and form a colloidal dispersion. Copper and gold are added to glass to produce a rich ruby-red color. Selenium also gives a beautiful red color to glass and is used both to produce this color and (in smaller percentages) to compensate for the green of ferrous silicate. Opaque, or milky, glasses are made by adding materials which remain suspended as solids in the melt, or which melt along with the glass but do not mix with it. In the latter case an emulsion is formed, and the turbid glass remains opaque on cooling. Fluorite, cryolite, calcium phosphate, and tin oxide are the most common materials added to produce that effect.

Special glasses. It should be kept in mind that the applications of glass in the arts and industries are increasing all the time. Each new application is apt to present a new problem to be solved by modifying the composition of the glass, or by manipulating it during manufacture, so as to give it properties exactly suited to the new use. Many such problems have been solved, but some still await solution.



Corning Glass Works

FIG. 342. *Glass-Blower Making a Condenser*

Optical glass. Until the early part of the present century, Germany supplied the United States with the special glass used in making lenses for microscopes, cameras, field glasses, and other optical instruments. During the war of the second decade it was necessary to develop production in this country and with the utmost speed. It was not difficult to learn the exact composition of optical glass by analysis. The trouble lay partly in the difficulty of securing pure materials, not only for the glass itself but also in the construction of the glass-pots in which the glassmaking is carried out, and partly in discovering the proper mechanical methods for carrying on the operation. For, if any iron is present in the materials, the resulting glass has some color, while if the operation is not carried on in the right way, the glass is not homogeneous; and either of these defects is fatal for optical glass. The problem was solved successfully, and the United States now produces optical glass in excess of its needs.

Glass transparent to ultraviolet light. Glass is transparent to light but it absorbs most of those waves beyond the visible violet of the spectrum called *ultraviolet light*. These waves have the greatest chemical and germicidal value, and the sunlight that comes to us through glass windows has but a small part of the value of direct sunshine. Pure silica glass transmits

this ultraviolet light, but it is very expensive and can be made in small pieces only. Much progress has been made in the production of a cheap glass that transmits ultraviolet light, and transparent resins have been developed that accomplish the same purpose.

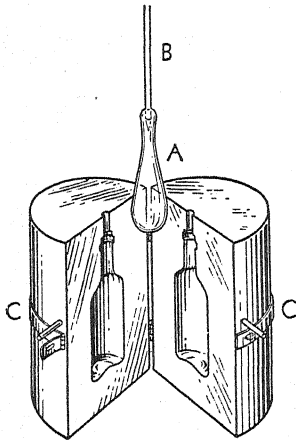


FIG. 343. *Making a Glass Vessel in a Mold*

Molding and blowing of glass. The way in which the melted mixture is handled in the glass factory depends upon the character of the article to be made. Some articles, such as ornaments and complicated chemical glassware, are mouth-blown directly into the finished product (Fig. 342). This requires great skill that can only be attained by years of practice. Many other articles, such as bottles, are made by blowing the plastic glass, either by the mouth or by compressed air, into hollow molds of the desired shape. The mold is first opened, as shown in Fig. 343. A lump of plastic glass *A* on the hollow rod *B* is lowered into the mold, which is then closed by the handles *C*. By blowing into

the tube the glass is expanded into the shape of the mold. The mold is then opened and the object lifted out. The neck of the object must be cut off at the proper place and the sharp edges rounded off in a flame. Bottles are now made chiefly by machines that produce the finished product entirely by mechanical means. The first of these machines was devised by Michael J. Owens in 1899, but it was a rather crude device. Continued improvements have now brought these machines to such a high state of perfection that a single machine will turn out 100,000 bottles daily.

Other objects, such as lamp chimneys, tumblers, and beakers, are also made by molding. The glass is revolved while being blown into the mold so as to avoid the formation of a ridge where the mold closes. Electric-light bulbs, originally mouth-blown, are now produced by machines brought to such a state of perfection that two machines will turn out more than 1,000,000 bulbs daily.

Window glass. Until recent times window glass was made by blowing plastic glass into long cylinders which were cracked lengthwise, heated until soft, and then flattened into sheets in much the same way as a cylindrical tube of paper, when cut lengthwise, will open to form a flat surface. This method has given way to other devices by which liquid glass is worked directly into continuous sheets that

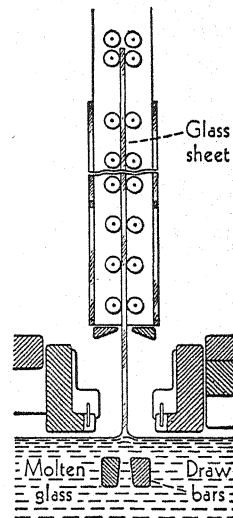
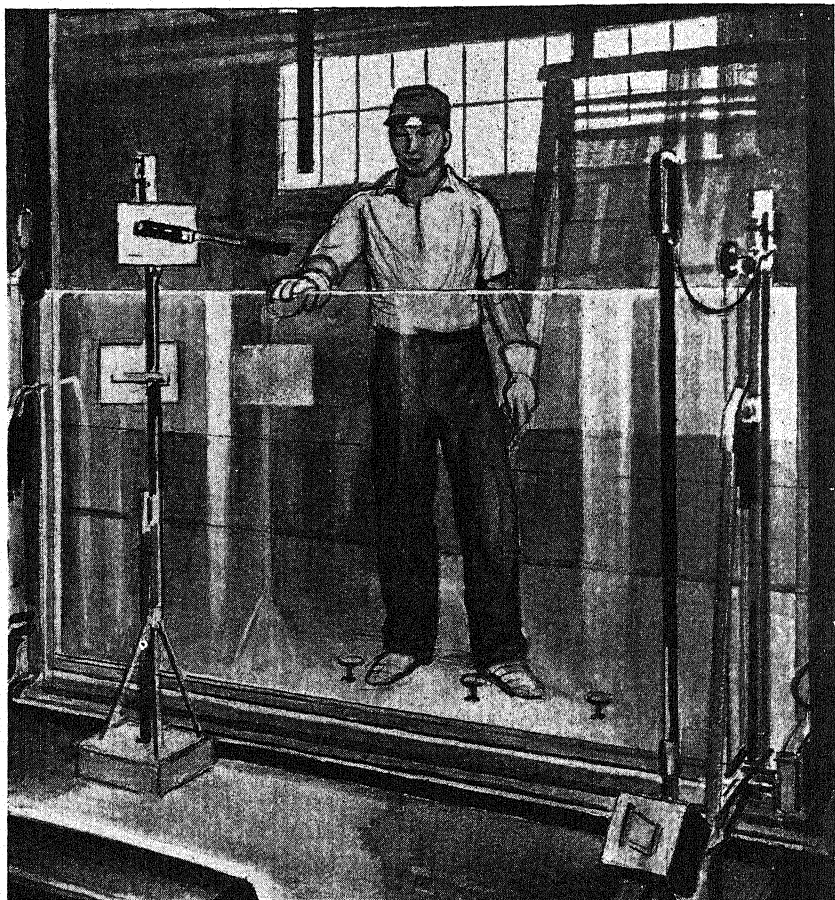


FIG. 344. *Drawing Sheets of Glass from Molten Glass*



Pittsburgh Plate Glass Company

FIG. 345. *The Manufacture of Window Glass*

View of the sheet as it emerges from the top rollers (see Fig. 344)

are then cut into desired sizes. Several methods are used for doing this but the principal one is the following :

The raw materials are put into a large furnace lined with refractory brick, and then heated with producer gas (or some other gaseous fuel) until the reaction is complete and the glass is in the form of a viscous liquid. To start the operation, a thin steel band (called the bait) is lowered into the glass and slowly withdrawn. The viscous glass adhering to the bait draws a continuous sheet of thick plastic glass upward between rollers, as shown in Fig. 344. As the sheet advances (25 ft or more), it cools, and emerges from the top rollers as a solid sheet that can be cut into the desired sizes (Fig. 345).

When once started, the operation continues during the life of the furnace (ten months or more). Raw materials are fed into one end of the furnace, and the melted glass is removed from the other end. Enormous quantities of window glass are required to meet the demand. Silverman states that the window glass manufactured yearly is sufficient "to pave a boulevard around Mother Earth at the equator eight lanes wide."

Plate glass. This form of glass is too thick to be made like ordinary window glass. A common method of making it consists in feeding plastic glass between a set of rollers from which it emerges horizontally onto a smooth surface. When cooled, it is polished, first with fine sand, and then with an oxide of iron known as "rouge."

Shatterless (safety) glass. This kind of glass, now largely used in automobiles, owes its chief property to its construction rather than to its composition. It is prepared by putting a sheet of certain plastics between two plates of glass and heating the combination under pressure.

Glass bricks. These are coming into use as a building material. The bricks are hollow, and are made by cementing together two half-bricks. Houses built of them require no windows, as the brick walls are fashioned so as to admit the proper amount of diffused light (Fig. 346). They are especially adapted for building houses that are air-conditioned.

Glass fibers. One of the latest developments in glassmaking is that of fashioning glass in the form of filaments so small that a large number of them are required to form a fiber no larger than an ordinary thread. The tensile strength of these fibers is comparable to that of steel. They are now produced in two forms, the one adapted for heat insulation, and the other for weaving fabrics, such as table linen and window curtains (Fig. 346). The manufacturers of this material state that "the length of insulating wool fibers produced in one hour on one glass machine is more than 100 times the distance around the earth at the equator."



Owens-Corning Fiberglas Corporation

FIG. 346. *The Walls of the Room Are Made of Glass Bricks and the Draperies of Glass Fabric*

Invisible glass. At least 8 per cent of the light that strikes the ordinary window glass is reflected from its surface. It is because of this fact that the glass in our windows is visible. Recent experiments have shown that glass becomes invisible when coated with an exceedingly thin film of certain materials, such as sodium and magnesium fluorides or a particular kind of soap. To produce this effect, the films must have just the right thickness so that the reflected wave of light will be exactly neutralized by oncoming waves. Glass so treated would seem to have important uses in the construction of certain optical instruments. Whether or not invisible window glass is desirable is an open question.

Annealing of glass. Melted glass, when cooled quickly, becomes very brittle. For this reason, glass articles, always hot when first fashioned, are cooled slowly, generally by passing them through a long furnace the temperature of which gradually diminishes from one end to the other.

CEMENT

Properties of cements. The term *cement*, in its broadest sense, is applied to any material which, mixed with water, forms a paste that becomes hard and durable on standing. These properties make it a useful material for many purposes, especially for joining bricks and stones and for building construction in general. Mixed with sand and crushed stone, it forms *concrete*, largely used in the foundations of buildings, road construction, dams (Fig. 347), and similar structures. Where great strength is required, iron rods or wire is embedded in the concrete before it sets, and this is known as *reinforced concrete*.

There are many different kinds of cements, but the most important and the most largely used is the so-called Portland cement. This has the additional advantage of hardening under water.

Portland cement. The material called Portland cement has long been known. The Romans used a similar cement at an early date, for building water conduits and as foundations for buildings and other structures. Its durability is shown by the fact that many of these conduits and foundations still exist in fairly good condition. The first real Portland cement was made in England in 1824 and was named because of its resemblance to a natural rock found on the Isle of Portland. Portland cement was first made in the United States in 1872, when a plant was built in the Lehigh valley, Pennsylvania. The industry, slow in development, gradually advanced until, in 1938, the production amounted to more than 100,000,000 barrels — an amount far greater than that produced in any other country (Fig. 347).

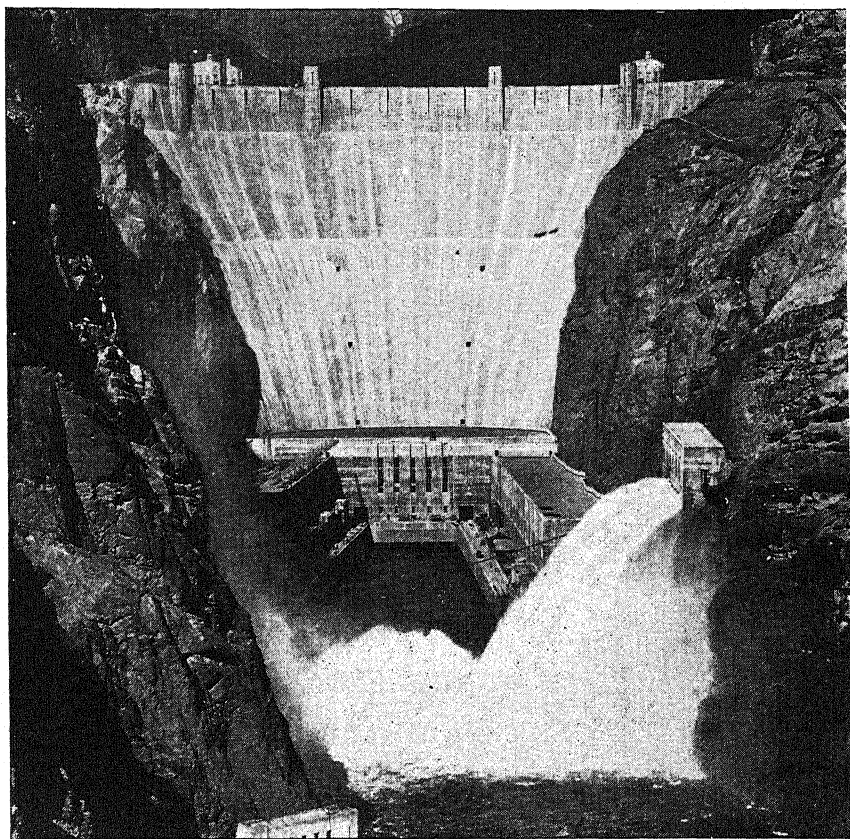


FIG. 347. *A View of Boulder Dam*

Some idea of the amount of concrete used in construction of dams is shown by the fact that the concrete used in building Boulder Dam would be sufficient to build a standard paved highway, 16 feet wide, extending from Miami, Florida, to Seattle, Washington

Manufacture of Portland cement. The chief materials employed in the manufacture of Portland cement are limestone, clay, shale, blast-furnace slag, marl, iron ore, and gypsum. The materials are coarsely ground, then mixed together in the proper proportions and finely pulverized. The resulting mixture is run into a rotary kiln (Fig. 348) and heated to a temperature just short of fusion, at which temperature it vitrifies and forms a grayish mass called *clinker*. The process of silicate formation is not so complete as in the case of glass, but definite compounds are formed. Finally the clinker is ground and mixed with a definite percentage of gypsum, which regulates the rate of setting of the cement when mixed with water.

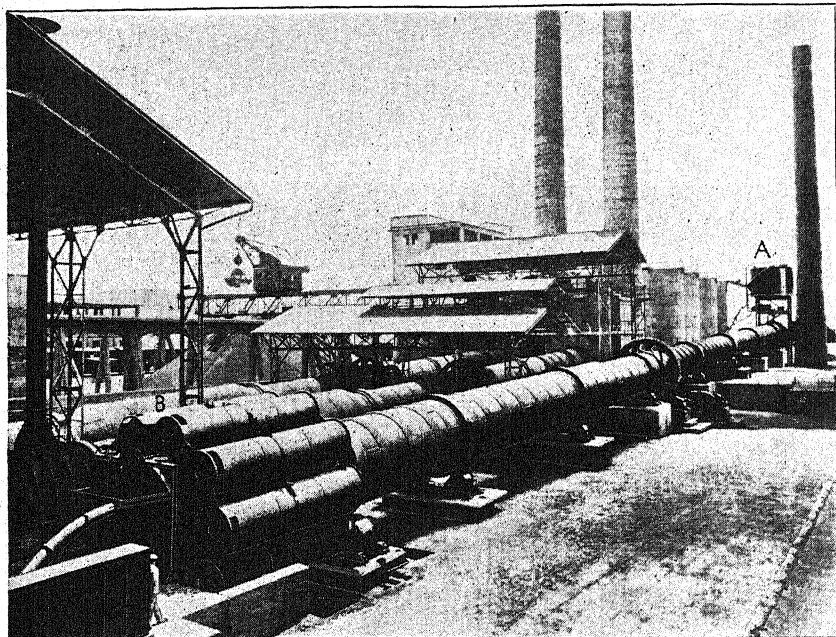


FIG. 348. *View of a Rotary Kiln Used in Making Cement*

The tube (kiln), about 300 feet long, constantly rotates. It slopes down from the far end A, where the raw materials are fed in, to the near end B, so that the materials slowly move forward from A to B, where the burnt clinker is removed. The fuel (gas, sprayed oil, or coal dust) burns with a hot flame as it enters the kiln at B, so that the cement materials are increasingly heated until they near the exit at B

The composition and setting of Portland cement. The composition of a material made of so many natural products varies rather widely but must be kept within certain limits. The chief compounds present in Portland cement, together with the time of setting of each, are as follows:

Components of Portland Cement and Time of Setting

COMPOUNDS	TIME OF SETTING
Dicalcium silicate, $2 \text{ CaO} \cdot \text{SiO}_2$	28 days
Tricalcium silicate, $3 \text{ CaO} \cdot \text{SiO}_2$	7 days
A mixture of the following aluminates: $3 \text{ CaO} \cdot \text{Al}_2\text{O}_3$ and $4 \text{ CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$	1 day

The reactions which take place in the setting of cement are not entirely understood. Apparently the compounds present undergo hydrolysis in contact with water, and the resulting compounds unite

with water to form hydrates, which produce the hard compact mass. The process of setting takes place best in air; but when the process is wholly or partially completed, the mass may be placed under water, since the compounds present are all insoluble.

Other kinds of cement. The quick-setting cements rather widely used are made by heating a mixture of bauxite and limestone and grinding the resulting mass to a fine powder. They consist of complex calcium aluminates, which set more quickly than Portland cement (see the table above). They are not as permanent as Portland cement but serve when quick setting is important. Another quick-setting cement is composed of tricalcium silicate, which sets in seven days as contrasted with the twenty-eight days required for the average Portland cement.

The so-called *oxychloride cements* are composed largely of the compound $3 \text{MgO} \cdot \text{MgCl}_2 \cdot 10 \text{H}_2\text{O}$. They differ from Portland cement in that they are quite elastic and are especially adapted for making floors. An admixture of powdered metallic copper improves these cements. There are many varieties of dental cement. A common kind is made by mixing zinc oxide with phosphoric acid.

CLAY PRODUCTS

Brick and draintile. The crudest forms of clay products, such as porous brick and draintile, have little chemistry involved in their manufacture. The clay is molded into the required form, dried, and then fired in a kiln, but not to a temperature at which the materials soften. In this process the nearly colorless ferrous compounds in the clay are converted into ferric compounds, which give the usual red color to these articles. In making vitrified brick the temperature is raised to the point at which fusion begins, so that the brick is partially changed to a kind of glass. Insulators for electrical wiring and spark plugs are special types of ceramic products.

White pottery. This term is applied to a variety of articles ranging from the crudest porcelain to the finest chinaware. While the processes used in the manufacture of the articles differ in details, fundamentally they are the same and may be described under three heads: (1) the preparation of the body of the ware, (2) the process of glazing, and (3) the decoration.

1. *The body of the ware.* The materials used consist of an artificially compounded body made from kaolin, plastic clay, pulverized quartz (known as Potter's flint), and pulverized feldspar. This mixture is plastic and is worked into the desired shape by molds or on a potter's wheel. The ware is then dried and fired to the desired density, and in this form is known as *bisque*. This is usually porous and must be glazed to render it nonabsorbent.



FIG. 349. *The Manufacture of Porcelain Plates and Similar Wares*

The picture shows the burning of the wares in a kiln. Various kinds of kilns are used; the one shown is circular in shape. The wares are placed on shelves that slowly revolve through a highly heated kiln

2. The glaze. The glaze is a fusible glass which is melted over the surface of the body. The constituents of the glaze are quartz, feldspar, limestone, clay, and various metallic oxides, often mixed with a little boric oxide. These materials are finely ground and mixed with water to a paste. Sometimes they are first fused into a glass, which is then powdered and made into the paste. The bisque is dipped into the glaze paste and then fired until the materials composing the glaze fuse and produce a smooth, glossy surface. The glaze must be so chosen as to resist the reagents to which it is to be exposed, and it must have the same coefficient of expansion as the body; otherwise it will check, or crackle, when the vessel is exposed to changes of temperature. It is evident that the calculation of a glaze for a given body requires a very thorough knowledge of the physical constants of the materials from which the body was made, as well as of the properties contributed to the glaze by each ingredient (Fig. 349).

3. The decoration. If the article is to be decorated, the design may either be painted upon the body before glazing, when it is said to be underglazed, or it may be painted upon the glaze and the article fired again, so that the pigments melt into the glaze. In the latter case it is said to be overglazed. In the former case the pigments used are, as a rule, metallic oxides, while in the latter case they are often colored glasses.

Enamels. Enamels are glazes applied to surfaces of various kinds, chiefly metals, to produce a smooth, vitreous, opaque surface which protects the body of the ware from rust. Graniteware cooking utensils, and plumbing accessories (such as bathtubs), are familiar illustrations. The enamel must be designed to correspond to the coefficient of expansion of the metal to which it is applied through the range of temperature to which it will be exposed; otherwise it will crack. It must also adhere firmly to the surface.

Tableware made from synthetic resins (plastics). Attention has been called to the many uses of plastics. They are especially adapted for making certain grades of tableware, for they are not easily broken and may be readily decorated and colored.

Questions

1. What is the difference between kaolin and clay?
2. Why does glass sometimes have bubbles in it?
3. Is the glass of an automobile windshield really "nonshatterable"?
4. (a) Why not use sodium phosphate in making glass rather than sodium sulfate? (b) Why not sodium chloride? (c) Why not sodium nitrate?
5. What are the reactions that take place when glass is made from sodium sulfate, carbon, and sand?
6. Does the statement that ordinary window glass "approximates the formula $\text{Na}_2\text{O} \cdot \text{CaO} \cdot 6 \text{SiO}_2$ " imply that glass is an impure compound?
7. If water should act upon ordinary window glass, what reactions should you expect to take place?
8. Why will ordinary mortar not set under water?
9. What are some of the properties that must be possessed by the porcelain that surrounds the wire of an automobile spark plug?
10. Why are telegraph wires strung on glass supports, while high-tension wires are carried on porcelain? Why not use porcelain supports for both?

Problems

1. To make glass of the composition corresponding to the formula $\text{Na}_2\text{O} \cdot \text{CaO} \cdot 6 \text{SiO}_2$, in what proportion must the following ingredients be brought together: sodium sulfate, calcium carbonate, sand?
2. Suppose you desired to make 1 kg of a hard glass of the Pyrex type and of the following composition: SiO_2 , 80 per cent; B_2O_3 , 12 per cent; Al_2O_3 , 3 per cent; Na_2O , 5 per cent. Suppose that the available materials are SiO_2 , B_2O_3 , $\text{Al}_2\text{Si}_2\text{O}_7$, and $\text{Na}_4\text{B}_2\text{O}_7$. What weight of each will be required?

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CHAPTER 35

The Iron Family

ELEMENT AND SYMBOL	ATOMIC WEIGHT	ATOMIC NUMBER	DENSITY	MELTING POINT	ELECTRONS IN SHELLS
Iron (Fe)	55.85	26	7.86	1535°	2:8:14:2
Cobalt (Co)	58.94	27	8.9	1480°	2:8:15:2
Nickel (Ni)	58.69	28	8.90	1452°	2:8:16:2

The family. The relationship among iron, cobalt, and nickel is different from that existing among the members of any family so far considered. Their atomic weights are very close together, and in the periodic table they are placed in one family because they are very similar and evidently constitute a natural group. They are *transitional elements* in the middle of the first long period (p. 213).

IRON

Occurrence. Iron has been in use as a metal for over four thousand years, since its ores are very abundant and it is not difficult to prepare the metal from them in fairly pure form. It occurs in large deposits as oxides, sulfides, and carbonates, and in smaller quantities in a great variety of minerals. Indeed, iron in small percentages is present in most rocks and soils, and it is assimilated by both plants and animals. It is a constituent of hemoglobin, and plays a fundamental part in life processes.

Preparation of pure iron. Pure iron may be prepared in the form of a fine powder by heating the oxide in a current of hydrogen, though the product contains adsorbed hydrogen unless the process is carried out at a high temperature. It may be obtained in coherent masses by the electrolysis of ferrous sulfate between iron electrodes. To prevent the adsorption of hydrogen, which makes the metal hard and brittle, it is necessary to conduct the electrolysis at about 100°, to add some calcium chloride to the electrolyte, and to heat the product for some time in a vacuum. By such methods Burgess has obtained iron said to be 99.98 per cent pure, and iron of nearly this quality can now be obtained commercially.

Properties of pure iron. Pure iron is a silvery metal having a density of 7.86 and a melting point of 1535°. It is ductile and malleable and is about as hard as an ordinary wire nail. It is especially well adapted to the manu-

facture of armatures and field pieces for dynamos and motors, since it acquires and loses magnetism much more rapidly than the ordinary varieties of iron.

The iron of commerce. Pure iron is rarely prepared and is of limited application, while iron which contains other elements exhibits a wide variety of properties and is of the greatest importance. Carbon is always present in quantities which range from mere traces up to 4.5 per cent. According to the conditions under which the metal is produced, this carbon may be in the form of graphite scattered through the iron, or as a solid solution of carbon in iron, or in combination with the iron in the form of a carbide. The most important of these carbides has the formula Fe_3C and is a hard, brittle substance known as *cementite*. In addition, manganese and silicon, together with traces of phosphorus and sulfur, are usually present.

The properties of iron are greatly modified by the percentages of these and other constituents, by their form of combination in the iron, and by the treatment of the metal during its production from the ore. The varieties of iron recognized in commerce are *cast iron*, *wrought iron*, and *steel*.

The metallurgy of iron. The problem to be solved in the production of commercial iron is (1) to obtain a metallic alloy of the requisite chemical composition and physical properties and (2) to produce it on a very large scale. The iron ore is first processed in a *blast furnace*, and the resulting crude iron either is finally made into cast iron (and an extremely small fraction into wrought iron) or is further treated in *Bessemer converters*, or in *open-hearth* or *electric furnaces*, to make steel. The development of the huge modern furnaces has demanded a wonderful application of chemical knowledge to a definite purpose, and a no less wonderful exercise of engineering skill in securing the present great scale of production. Let us now trace the various stages of the metallurgical processes, from iron ore to final product.

World iron-ore supplies. The principal iron-bearing minerals of the world, suitable as ores, are the following:

Iron-bearing Minerals

MINERAL	FORMULA	IRON IN PURE MINERAL
Hematite	Fe_2O_3	70.0 per cent
Magnetite	Fe_3O_4	72.4 per cent
Limonite	$x \text{Fe}_2\text{O}_3 \cdot y \text{H}_2\text{O}$	52.3 — 66.3 per cent
Siderite	FeCO_3	48.3 per cent

These minerals seldom occur pure in large quantities, but are found mixed with earthy substances, especially silica (and silicates), and often with sulfides and phosphates as well.

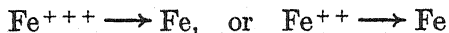
Many countries have high-grade iron-ore deposits: the United States (near Lake Superior and around Birmingham, Alabama), England (in Cumberland and Lancaster), France (in Lorraine), Sweden, Chile, Brazil, and Germany. Italy, Spain, India, and Russia have good deposits.

Production of iron ore. While the production varies from year to year, an average of about 50,000,000 tons of iron ore is mined annually in the United States. About 80 per cent of this comes from the great Mesabi Range in the Lake Superior region, and represents about 40 per cent of the world's production. The output of the Lorraine mines is also large. In a normal year the very pure Swedish magnetite ore (about 70 per cent iron), which is used to make a fine-quality iron, is mined to the extent of about 8,000,000 tons. Germany normally mines about 6,000,000 tons. Fifteen countries each produce as much as 1,000,000 tons a year; but a small mine on the Mesabi Range will do as well. Mining engineers estimate that the world's high-grade iron ores are nearing exhaustion (except in Brazil). If this is true, we may soon become dependent on the leaner-grade ores or on the *marginal ores* or on the so-called *formation materials* (silicate rocks carrying relatively small percentages of iron-bearing minerals).

Blast furnaces in the United States. After being mined on the Mesabi Range, the various grades of the *hematite ore*, following some washing and "jigging" to concentrate the leaner ores, are blended to give a uniform stock containing 51.5 per cent iron; and this is shipped in lake boats during the eight-month season through Sault Sainte Marie to the various lake ports for delivery to blast furnaces. Most of our blast furnaces are located in a few states. In 1938 there were 78 in Pennsylvania, 48 in Ohio, 23 in Illinois, 20 in Alabama, 19 in Indiana, 17 in New York, and 8 in Michigan; the rest of a total of 236 were scattered among fourteen other states. The blast furnaces of Alabama and of some other states are supplied with ore mined in their own locality.

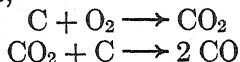
The metallurgy of the blast furnace. There are three primary functions of the blast furnace:

1. The first function is to reduce the ionic iron in the iron ore to metallic iron:



This is done by heating the ore with the reducing agents, solid carbon (coke, coal, or charcoal) and carbon monoxide gas. The final iron obtained is called *pig iron*. At least 99 per cent of the pig

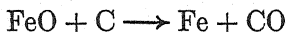
iron throughout the world is made with coke. The coke is not only one of the reducing agents, but also the fuel which burns and generates most of the heat. The probable chemical reactions are, first, the formation of carbon dioxide and carbon monoxide near the bottom of the furnace,



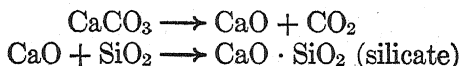
and, second, the partial reduction of the iron ore (say hematite) by carbon monoxide,



followed by the complete reduction by the hot coke



2. The second function is to dispose of the impurities of the ore and the ash from the coke. This is accomplished by adding a *flux* to the furnace charge to form a *slag* with the impurities. Since silica is generally the predominant impurity in the ore, limestone (CaCO_3) is usually employed as the flux:



If oxides more basic than SiO_2 , like Al_2O_3 , are present in the ore or ash, they also react with the lime and silica to form a fusible, glassy silicate slag.

3. The third function is to separate the metallic iron from the slag. The ore itself can be reduced at a temperature considerably below the melting point of iron. But the best way to separate the iron from the slag is to maintain a temperature hot enough to melt them both, at the bottom of the furnace, and allow them to separate automatically by virtue of their greatly different densities.

Details of the blast-furnace process. The modern blast furnace is a tower (Fig. 350) about 95 ft high and 24.5 ft in internal diameter at its widest part, narrowing somewhat toward both the top and the bottom. The walls are built of steel and are lined with firebrick. The base is girdled with a pipe *A, A*, through which a blast of hot air is forced. Leading from this are smaller pipes *B, B*, called *tuyères*, which conduct the blast of hot air into the furnace. At the base of the furnace is a taphole *K* for the molten iron, through which the liquid metal can be drawn off from time to time by the conduit *C*. There is also a second opening *L*, somewhat above the first, through which the excess of molten slag is drawn off by the conduit *D*. The

top is closed by a movable trap *G*, called the *bell*, and through this the materials to be used are introduced. The gases resulting from the combus-

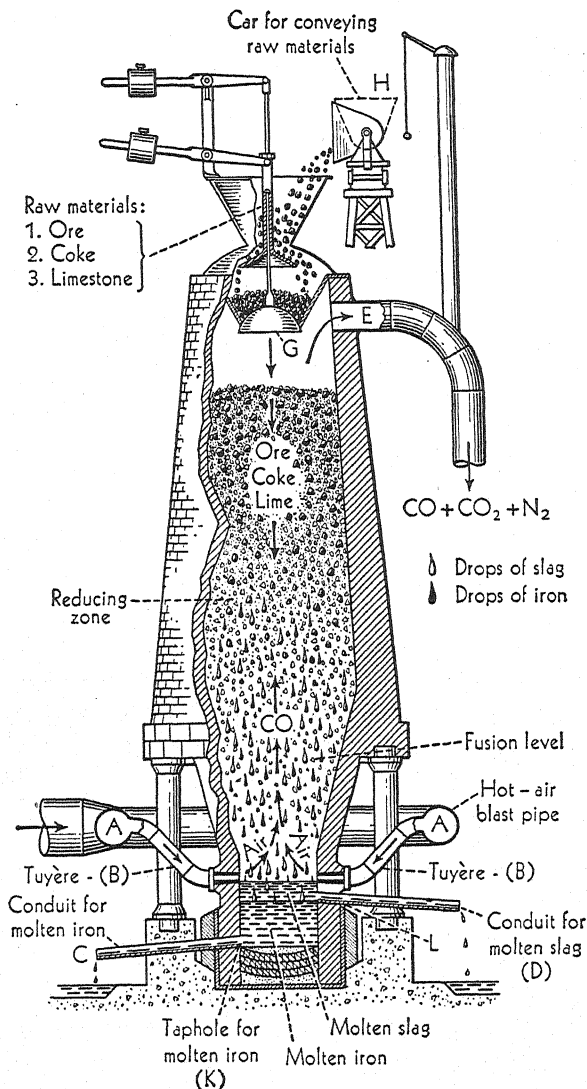


FIG. 350. Vertical Section of a Typical Blast Furnace

tion of the fuel and the reduction of the ore, together with the nitrogen of the air admitted through the tuyères, escape through pipe *E*. These gases have a temperature of about 300° and contain a sufficient percentage of carbon monoxide to render them combustible; they are accordingly utilized

for heating the blast of air admitted through the tuyères and as fuel for the engines.

Charges consisting of coke, ore, and flux, in proper proportions, are at intervals introduced into the furnace through the bell. At the bottom of the furnace the coke burns fiercely in the hot-air blast, forming carbon dioxide, which is at once reduced to carbon monoxide as it passes upward through the highly heated carbon.

The temperature of the furnace at the point at which the hot air enters is about 1600° , but gradually decreases toward the top of the furnace, where it is only from 300° to 400° . Reduction of the ore begins at the top of the furnace through the action of the carbon monoxide. As the ore slowly descends, the reduction is completed by the coke, and the resulting iron melts and collects as a liquid in the bottom of the furnace, the lighter slag floating on top of it. After a considerable quantity of iron has collected, the slag is drawn off, and the iron is run out into large buckets and taken to the converters for the manufacture of steel; or it is run into iron troughs or molds lined with lime and connected in the form of an endless chain and cast as "pigs." The process of producing pig iron is a continuous one; when the furnace is once started, it is kept in operation for months without interruption, or until the furnace requires repairing. The iron is withdrawn at intervals of about six hours.

Pig iron. As it comes from the blast furnace, pig iron is the intermediate raw material from which all other varieties of iron are made. Because of excessive impurities and because the rate of cooling cannot be well controlled, it is weak and brittle and not fit for any other than very crude uses until refined. A fairly representative analysis (expressed in percentages) is as follows: C, 3.50; Si, 2.00; Mn, 0.80; P, 0.15; S, 0.04. In the year 1938 about 18,600,000 tons of pig iron was produced in the United States.

Cast iron. Cast iron is made from pig iron by a very simple process. A charge of pig iron, together with scrap iron of better quality (and sometimes other materials), is melted in a small furnace called a *cupola* furnace. The liquid metal is cast in sand molds, and the rate of cooling is carefully controlled, since this has much to do with the state of the carbon in the finished casting.

Cast iron varies considerably in composition but always contains over 2 per cent of carbon, variable quantities of manganese and silicon, and at least traces of phosphorus and sulfur. Two extreme varieties of cast iron are recognized: *gray* iron and *white* iron. In gray iron (slow cooling) the carbon is present partly in the form of *cementite* (Fe_3C) and partly as *graphite*, which gives the metal its gray color. In white cast iron (rapid cooling) almost all the carbon is in the combined state in the form of cementite. Cast iron is hard

and brittle and melts at about 1100°. It cannot be welded or forged, although it can now be made malleable by a special treatment which converts all the cementite into graphite. It is rigid but not elastic, and its tensile strength is small. It is used for making castings which require no great strength, such as those for stoves, radiators, bases for machinery, and engine blocks. Cast iron, especially those grades of high silicon content, is not acted upon by acids to the same extent as the purer grades of iron and so is used in making vessels for concentrating acids and for similar purposes.

Wrought iron. An old process for radically improving pig iron was to convert it into *wrought iron* by using iron oxide, in the presence of a flux, to burn out most of the carbon, silicon, phosphorus, and sulfur from the pig iron, in furnaces known as *puddling furnaces*. As the iron is freed from other elements, it becomes pasty, owing to the higher melting point of the purer iron, and in this condition forms small lumps, which are raked together into a large one stuck together by the viscous slag. The large lump is then removed from the furnace and rolled or hammered into bars, with most of the slag squeezed out in this process.

A much more rapid process is displacing the puddling furnace. This consists in pouring a pure grade of iron (known as Bessemer iron) into a prepared, melted slag and mixing the two together. This material is cast into ingot molds and is then rolled and hammered until the excess slag is squeezed out. The resulting iron has exactly the same physical structure as that made in the puddling furnace. Wrought iron has a fibrous structure, for it is composed of elongated grains of pure iron (*ferrite*) interspersed with elongated granules of slag. The ferrite present contains less than 0.3 per cent of carbon and small amounts of other elements. Wrought iron is soft, malleable, and ductile. While its tensile strength is greater than that of cast iron, it is less than that of most steel. Its melting point is much higher than that of cast iron. Wrought iron is no longer produced to the same relative extent as in former years, but its *actual* production tends to increase somewhat, owing to its resistance to rust and corrosion.

STEEL

General. Steel, like wrought iron, is made from pig iron by burning out a part of the carbon, silicon, phosphorus, and sulfur, but the processes used are very different and the scale of production vastly different. Nearly all the steel of commerce produced in the United States is made by one of two general methods, known as the *acid Bessemer process* and the *basic open-hearth process*.

Acid Bessemer process. In the acid Bessemer process the furnaces used are lined with *silica*, which, it will be recalled, is an *acid an-*

hydride. These furnaces remove from the pig iron the carbon, manganese, and silicon, but the acid lining cannot withstand the *basic* slag needed to remove the phosphorus and sulfur. The process is therefore employed when the pig iron used is, like some American pig iron, low in phosphorus and sulfur.

Details of operation of the Bessemer process. This process, which was invented in 1855 by Bessemer and which gave the world its first low-priced steel, is carried out in great egg-shaped crucibles called *converters* (Fig. 351), each one of which will hold as much as 25 tons of steel. The converter is built of steel and lined with silica. It is mounted on trunnions, so that it can be tipped over on its side for filling and emptying. One of the trunnions is hollow, and a pipe connects it with an air chamber A, which forms a false bottom to the converter. The true bottom is perforated, so that air can be forced in by an air blast admitted through the trunnion and the air chamber.

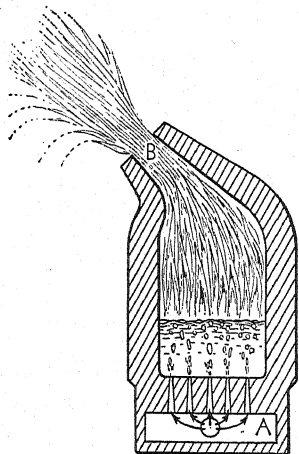
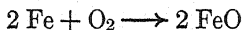


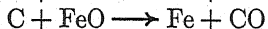
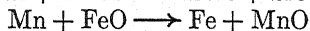
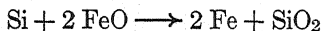
FIG. 351. Vertical Section Showing Details of a Bessemer Converter

White-hot liquid pig iron from a blast furnace is run into the converter through its open, necklike top B, with the converter tipped over to receive it; the air blast is then turned on, and the converter is rotated to a nearly vertical position. The carbon, manganese, and silicon in the iron are rapidly oxidized (first the silicon and manganese and then the carbon), but not directly by oxygen.

Some of the iron is oxidized,



and then this dissolved iron oxide reacts with the other elements:



The oxidation is attended by a brilliant flame. The heat of the reaction, largely due to the combustion of silicon, keeps the iron in a liquid condition. If the charge becomes too cold, more silicon, in the form of an iron-silicon alloy, may be added; if it gets too hot, it may be cooled down by throwing in cold scrap iron. The air blast is continued until the character of the flame shows that all the carbon has been burned away. The process requires on the average about ten minutes; and when it is complete, the desired quan-

tity of carbon (generally in the form of high-carbon iron alloy or anthracite) is added and allowed to mix thoroughly with the fluid. The converter is then tilted and the steel run into molds, and the ingots so formed are hammered or rolled into rails or other objects. The process must be conducted very rapidly, for as soon as the silicon and carbon have been burned, the iron will begin to burn up; moreover, since there is then no way to keep the iron from cooling, it must be poured at once.

Bessemer steel is suited to many standard articles, such as rails and structural materials. It is sometimes cheaper than open-hearth steel but not adapted to such a variety of purposes.

Basic open-hearth process. In the basic open-hearth process the lining of the furnace is made of limestone or dolomite, both of which act as *bases*. In such furnaces most of the phosphorus and sulfur are removed, as well as the silicon and carbon. The presence of more than traces of phosphorus and sulfur in the finished steel renders the metal so brittle that it is worthless for most purposes. The open-hearth process, therefore, possesses a great advantage over the acid Bessemer process in that it makes it possible to utilize iron ores (or pig iron obtained from them) that contain appreciable quantities of phosphorus and sulfur. The operation does not need to be hastened, and steel of any desired composition can be produced.

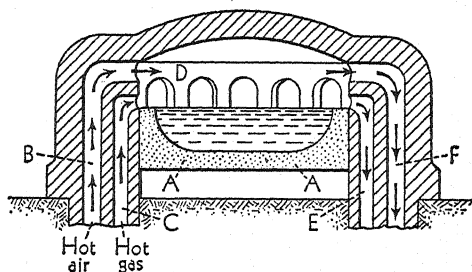


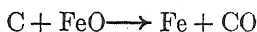
FIG. 352. *Cross Section of an Open-Hearth Furnace*

Details of the open-hearth process. Fig. 352 shows the simpler parts of the type of furnace used in this process. Open-hearth furnaces have capacities varying from about 50 to 500 tons of steel per melt, and two or three melts can be made daily. The hearth of a medium-sized furnace is about 40 ft in length, 12 ft in width, and 2 ft in depth, and is lined with magnesite (calcined magnesium carbonate) (A, A). Either gas or sprayed oil or finely powdered coal is used as fuel. Below the furnace is placed a checkerwork of brick so arranged that the hot products of combustion escaping from the furnace may be conducted through it, thus heating the bricks to a high temperature. Both the air necessary for combustion and the gaseous fuel (unless decomposed by heating, as in the case of natural gas and sprayed oil) are preheated by passing them over the hot bricks, so that the temperature reached during combustion is greatly increased. The gas entering

through *C* comes in contact at *D* with the hot air entering through *B*, and a vigorous combustion results. The flame passes over the charge in the furnace; and at regular intervals the direction from which the fuel and air enter the furnace is reversed.

Charging the open hearth and melting down. Into the open hearth are charged limestone, steel scrap, and pig iron, the last either hot or cold. Also *iron ore* is added, sometimes all the required amount at the beginning, but more usually only a part of it at first, and the rest after the slag is formed. The silicate slag, made up largely of CaO and of SiO_2 from the ore, and of oxidized silicon from the pig iron, eventually rises and covers over the molten steel. The slag plays an important role in the steelmaking process.

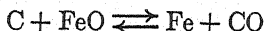
Chemical reactions in the open hearth. When the melt has come up to temperature about 1600° , control of the chemical reactions begins. Some iron oxide, from the ore, has already dissolved in the slag, and more is added as it is needed. The iron oxide passes, by diffusion, from the slag into the melt underneath, where it dissolves in the liquid iron, and oxidizes the silicon and manganese first and then the carbon, just as in the Bessemer process. The oxides of silicon and manganese pass into the slag. The phosphorus, to the extent to which it is oxidized (probably to P_4O_{10}) is very likely locked in the slag by basic oxides, and the sulfur may in part be oxidized and escape as a gas or be locked in the slag. The carbon is oxidized,



and the carbon monoxide may be given off so rapidly that the melt and slag appear to "boil." The diminishing carbon content is followed by frequent sampling and rapid analysis; and when the percentage of carbon has been dropped to the required value, the melt is ready for pouring. However, before the furnace is tapped, the alloying elements, or elements with special functions, may be added, in weighed amounts, such as manganese, aluminum, silicon, chromium, nickel, vanadium, tungsten, and molybdenum. The function of these elements will be described later.

Pouring. The slag is removed and the molten steel allowed to run out of the furnace into a large bucket-shaped vessel (lined with refractory brick) called a *ladle*. (Sometimes the alloying elements are added in the ladle rather than in the furnace.) At this stage two different pouring practices may be followed.

1. The steel may be poured, as it is, from the ladle into ingot molds to form what is called *rimmed steel*. In this case, gas blowholes are formed in the solidified ingot. The reaction represented by the equation



is an equilibrium reaction, and the equilibrium is displaced toward the right as the steel cools. A very large quantity of carbon monoxide gas is set free

— not all of which escapes from the ingot. The blowholes, however, are partially or entirely healed by later rolling or drawing operations, and rimmed steel is generally used to make deep-drawn shapes, such as sheets.

2. Before being poured from the ladle (or from the furnace) the steel may be *killed*. This means that enough aluminum (or silicon, manganese, or titanium, generally in the form of its iron alloy) is added to combine with the oxygen of the FeO . These oxygen *scavengers* have a great affinity for oxygen, and their oxides are so stable that little, if any, carbon monoxide and no blowholes are produced.

Mill operations. When the steel ingot, whether rimmed or killed, has completely solidified, it is stripped out of the mold and heated for some time to a bright-red heat in a *soaking pit* (generally fired by gas) to relieve any strains that may have developed during the solidification process. The hot, plastic ingot then passes to the rolling mill, where it is worked down into various shapes by stepwise passes through steel rollers; or it may be drawn or sawed or forged. An idea of the relative amounts of the various general forms into which the approximately 32,600,000 tons of finished steel was fashioned in the United States in 1939 is given by Fig. 353.

Electric-furnace steel. A considerable quantity of high-grade alloy steel is made today in electric furnaces, generally of the arc type, in which the heat is generated in an arc that jumps between very large vertically placed graphite electrodes and the slag over the molten metal. The capacity of such furnaces is much smaller than the open hearth, and the control of the reactions somewhat closer. Otherwise the principles involved in the steelmaking are the same.

Growth of crystalline grains. When steel solidifies in an ingot, crystals of the metal are formed. These crystals start at nuclei, little clusters of atoms, and grow out in all directions by adding on atoms, until neighboring crystal grains meet, as shown in Fig. 354, in the successive stages 1, 2, 3. The lines in 4 indicate the grain boundaries. (Compare with the photomicrographs of Fig. 355.)

Into the grain boundaries are pushed many trace materials which are soluble in molten steel but not in the crystal grains. For in-

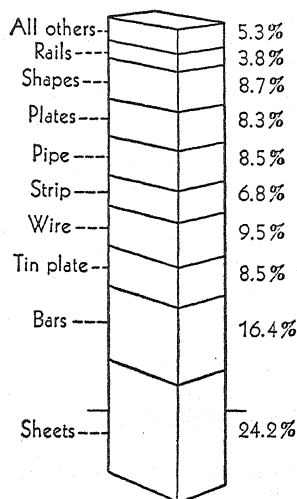


FIG. 353. Diagram Showing Percentage of Fashioned Steel Products in 1939

stance, iron sulfide, FeS , collects at the grain boundaries; and since it is *melted* at the temperature of rolling and forging, its presence as a liquid film causes the steel to crack and break up along the grain boundaries. This may be prevented by the addition of manganese in sufficient quantity before pouring. Manganese sulfide, MnS , is formed; and while this too is trapped in the grain boundaries, it is a solid which does not melt at the temperature of hot-working the steel. For this reason manganese is today regarded as an essential constituent of most steels.

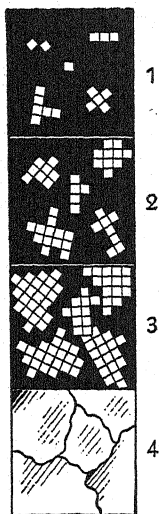


FIG. 354. Diagram Showing Crystal Grain Growth

Allotropy of iron. Like many other elements, iron has allotropic forms. (1) Alpha iron, or *ferrite*: Iron at ordinary temperatures is made up of grains which are crystals having a body-centered lattice (Fig. 313, A). (2) Gamma iron, or *austenite*: Above 910° the lattice changes to a face-centered form (Fig. 100). (3) Delta iron: Above 1390° (near the melting point of iron, 1535°) the lattice changes back to a high-temperature body-centered form.

The tempering and hardening of steel. When steel containing from 0.5 to 1.5 per cent of carbon is heated to a temperature above 910° and then cooled suddenly by plunging it into cold water or oil, it becomes very hard and brittle. When reheated to temperatures ranging from 220° to 320° and then slowly cooled, this hard steel becomes softer and less brittle, and the process is called *tempering*. All such articles as springs and cutting tools are tempered in this way, each at a temperature best suited to its use.

Soft steel is sometimes hardened merely on the surface by a process called *casehardening*. The object is heated in powdered carbon or in various materials that yield carbon. The carbon slowly dissolves in the steel and converts the surface layer into high-carbon steel.

The carbon is present as cementite, Fe_3C , and hardening and tempering are explained in terms of what happens to the cementite. This is completely soluble in austenite (gamma iron), but is *not soluble* in ferrite (alpha iron). If, however, the hot austenite is transformed suddenly into ferrite by a quick chill, the cementite does not have time to crystallize out and is held in supersaturated solution in the ferrite. Ordinarily ferrite is relatively soft and plastic. But the "stranger" Fe_3C molecules intrude themselves between the

layers of the ferrite lattice, dipping partly into one layer and partly into another, and "key" the layers together and prevent easy slippage of one layer over another. In this way the plasticity of the lattice is cut down, and the steel becomes brittle and extremely hard. Steel in this form is called *martensite*.

When the martensite is tempered by heating, the cementite precipitates out of the ferrite and builds little crystals of its own, thus leaving zones of soft ferrite in between the cementite crystals.

Alloy steels. Of all the alloying elements, carbon is the most influential in steel. By variation of its content and by suitable heat treatment, a remarkably wide range of properties (ductility, malleability, strength, toughness, hardness) is available. Often we may wish to have a steel which is very hard, but at the same time tough rather than brittle, or a steel which is resistant to corrosion or to mechanical shock. These extreme properties or combinations of properties can be achieved by alloying the carbon steel with other elements. For example, the addition of chromium to steel makes it tough even while hard. Tungsten will keep a steel hard at high temperatures, and is used in high-speed tool steels. Nickel and chromium are the most widely used of all the alloying elements.

Since any number of these metals may be added together and in any proportion, it is possible to make a steel alloy with almost any

Some Alloy Steels

PERCENTAGE COMPOSITION	PROPERTIES	USES
3.5 Ni	Hard, strong	Armor plate
3.5 Ni, 1.5 Cr	Hard, tough, strong	Armor plate, projectiles, objects enduring shock or strain
1.5 Ni, 0.6 Cr		
1-1.5 Ni, 0.2-0.7 Cr }		
17-18 W, 3.5-4.5; Cr Co, Mo, U in optional proportions	Hard and temper-holding at high temperatures	High-speed lathe tools
12 Mn	Strong, tough	Burglarproof safes
13 Cr, 0.35 C	Rust-resisting	Stainless cutlery
17-19 Cr, 7-9.5 Ni, 0.11 C	Stainless, great strength	Rollers, furnace parts, plant equipment
0.1 Ti	Hard	Car rails and castings
0.2 V, 3.5 Ni, 0.75 Cr, 0.4 Mn	Fatigue-resisting	Automobile springs and axles
12-15 Si (duriron)	Corrosion-resisting	Acid stills, electrodes
0.1 V	Tough	Automobile parts

* These are three standard nickel-chromium steels, the last one being made from a natural (Cuban) ore containing the three elements (Mayari ores).

given set of properties. Literally hundreds of these alloys have been made, and many of them have registered trade names, such as

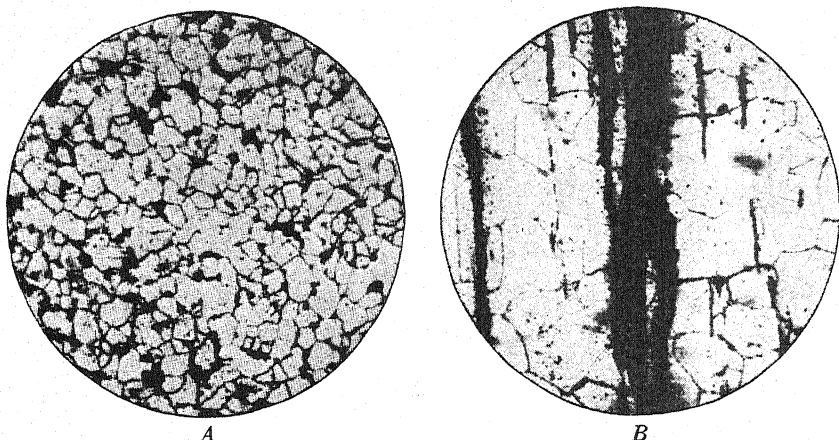


FIG. 355. *A is a Sample of Low-Carbon Steel, and B a Sample of Wrought Iron*

These two samples have nearly the same percentage composition, but their different methods of manufacture have resulted in entirely different physical structures with corresponding differences in properties

Duriron, a high-percentage silicon alloy that is very hard and brittle but resists acid corrosion. The remarkable hardness of such alloys as those of nickel, chromium, cobalt, tungsten, and vanadium arises by a situation similar to that previously noted for Fe_3C molecules. The "stranger" atoms intrude themselves between layers in the iron lattice and "key," or "lock," the layers together. The preceding table indicates the composition and properties of a few of the commonly used alloy steels.

Metallography. We have seen that the varieties of iron differ not only in chemical composition but also in physical structure. Much information concerning the structure of any sample of iron (and other metals as well) can be obtained from photomicrographs of carefully prepared specimens of the different varieties of iron. To prepare these, a cross section of the sample is made and polished. This is then etched with some reagent such as nitric acid, which will react upon the different constituents of iron with different speeds. The photomicrographs are then taken of the resulting surfaces. This method of studying the structure of metals is known as *metallography*. Fig. 355 shows two typical photomicrographs of this kind.

Passive iron. Iron readily dissolves in both dilute and concentrated nitric acid; but when it is brought into contact with fuming nitric acid, that is, with nitric acid containing nitrogen dioxide in solution, it loses many of its characteristic properties and is then said to be in a *passive state*

(Fig. 356). For example, such iron is no longer attacked by dilute nitric acid, nor does it precipitate copper and silver from solutions of their salts, as does ordinary iron. The metal loses its passivity when it is rubbed, scratched, or given a sharp blow, or when certain other metals are brought into contact with it. A number of other metals, including cobalt, nickel, and chromium, act in a similar way. No entirely satisfactory explanation has been offered to account for this phenomenon. Possibly the passivity is due to the presence of a protective film of oxygen on the surface of the metal.

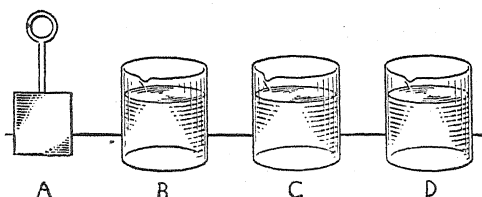


FIG. 356. *Diagram Illustrating the Preparation and Properties of Passive Iron*

The passivity of iron may be illustrated in the following simple way: A piece of sheet iron *A* is immersed for a few moments in fuming nitric acid contained in *B*. It is next lowered into pure water in *C*, in order to wash off the adhering acid. Finally, it is dipped for a moment into a solution of copper sulfate in *D*. Apparently no change takes place. If now the iron is struck a sharp blow, it at once loses its passivity and regains its normal property of replacing copper from copper sulfate, as is evidenced by the rapid formation of a thin film of copper over the entire surface of the iron.

ordinarily we think of atoms as being *spheres*; but the shape of any atom may depend to some extent on the environment in which it is found, and it is possible that the atoms of alpha iron are at least approximately cubes. This manner of piling atoms together is known as the body-centered cubic lattice because there is an atom at the center of every group of eight atoms at the corners of a cube, as one can readily see in Fig. 357.

It will be observed that there are tunnels running through this lattice, and in the lower right-hand corner of the figure there is shown a ball which represents the relative size of a hydrogen atom. A hydrogen *atom* is small enough to enter these tunnels, and this may be said to "explain" the well-known fact that atomic hydrogen is soluble in iron at ordinary temperatures. Hydrogen liberated electrolytically at an iron electrode or by the action of an acid on iron exists for a short interval of time as atoms (nascent state), before these have time to double up into molecules, and will diffuse as atoms into the tunnels of the lattice. The presence of this dissolved atomic hydrogen profoundly affects the physical properties of the iron, making it much more brittle.

Solution of atomic hydrogen in iron. In Fig. 357 the atoms of alpha iron are represented as little cubes. Ordinary

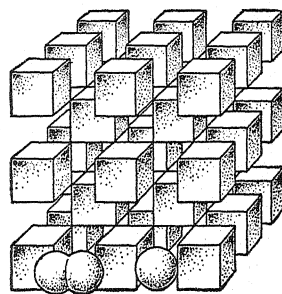


FIG. 357. *Crystal Lattice of Alpha Iron, with Atomic and Molecular Hydrogen*

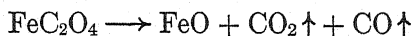
A *molecule* of hydrogen gas, shown at the left of Fig. 357 as a twin-atom dumbbell, is too large to get into the tunnels, agreeing with the fact that molecular hydrogen will not dissolve in iron. The presence of these tunnels accounts also for the diffusion of carbon in steel.

COMPOUNDS OF IRON

Two valence series. Iron differs from the metals so far studied in that it is able to form *two series* of compounds. In one series the iron is *bivalent* and forms compounds which in formulas and many chemical properties are similar to the corresponding zinc compounds. These are called *ferrous* compounds. In the other series iron acts as a *trivalent* metal and forms salts similar to those of aluminum. These salts are known as *ferric* compounds. Iron is also present in many complex salts.

Ferrous compounds. The ferrous salts resemble those of zinc not only in formula but often in degree of hydration. They are not greatly hydrolyzed in solution, for ferrous hydroxide is about as strong a base as the hydroxide of zinc; but they are readily oxidized, as will be explained later. The soluble salts (usually green in color) are easily prepared by dissolving iron in the appropriate acid, and the insoluble salts by precipitation.

Ferrous oxide (FeO); ferrous hydroxide ($\text{Fe}(\text{OH})_2$). Ferrous oxide may be obtained as a black combustible powder, by heating ferrous oxalate:

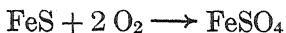


When a solution of a ferrous salt is treated with a soluble base, a white precipitate forms, which is a colloidal gel of the hydroxide, $\text{Fe}(\text{OH})_2$. If this is exposed to air and moisture, it quickly oxidizes to a hydrated ferric oxide.

Ferrous chloride (FeCl_2). Anhydrous ferrous chloride is prepared by strongly heating iron in a current of hydrogen chloride. The salt condenses in the colder portions of the tube in white pearly scales. It dissolves in water, with evolution of much heat, and from this solution there crystallizes the green tetrahydrate, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$. The latter salt is more easily obtained by dissolving iron in hydrochloric acid and crystallizing the solution out of contact with the air.

Ferrous sulfate (FeSO_4). The sulfate is the most familiar ferrous salt and has many uses. It is easily prepared by dissolving iron in dilute sulfuric acid and evaporating until crystallization occurs. It is then obtained in large monoclinic crystals of the composition

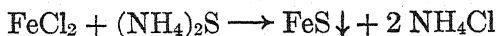
$\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$, known as *green vitriol*, or *copperas*. In the industries it is obtained from the liquors which result from cleaning sheet steel with sulfuric acid preparatory to tinning or galvanizing the steel. It is also manufactured by the oxidation of the abundant mineral pyrite (FeS_2), usually after a careful partial roasting, which converts the pyrite into ferrous sulfide (FeS):



It is used as a disinfectant, as a reagent for killing weeds, in the dyeing industry, as a substitute for aluminum sulfate in water purification, and in the manufacture of black inks.

The vitriols. The term *vitriol* is applied to the hydrated sulfates of a number of bivalent metals. These compounds are of two distinct types: the one group forms monoclinic crystals which contain 7 molecules of water of hydration; the other forms triclinic crystals with 5 molecules of water. All the salts in a given series are isomorphous, and many of the vitriols are dimorphous, crystallizing in both forms. The sulfates of iron, zinc, and magnesium are the most familiar representatives of the monoclinic vitriols, while copper sulfate ($\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$) is the best-known triclinic vitriol.

Ferrous sulfide (FeS). Ferrous sulfide is found in nature as the yellowish-brown mineral *pyrrhotite*, which nearly always contains an excess of sulfur in solid solution, amounting sometimes to as much as 6.5 per cent of the weight of the mineral. It is easily prepared by heating iron with sulfur or by treating a solution of a ferrous salt with a soluble sulfide:



Prepared in the latter way it is a black precipitate, insoluble in water but readily soluble even in very weak acids. It melts at about 1190° and is obtained as a liquid flux in some metallurgical processes. It is used in the laboratory in the preparation of hydrogen sulfide.

Iron disulfide (FeS_2). This compound occurs very abundantly in nature, especially in Spain. It is also found in the coal measures, often forming fossils of plants. The usual form is called *pyrite*, *pyrites*, or *fool's gold*, and is a brass-yellow mineral, well crystallized in the isometric system. Pyrite is mined in very large quantities and is used as a source of sulfur dioxide in the sulfuric acid industry.

Ferrous carbonate (FeCO_3). As *siderite*, isomorphous with calcite, ferrous carbonate occurs rather abundantly in nature, often in large crystals.

Prepared by precipitation, it is a nearly white crystalline powder. Like calcite, it is soluble in water containing carbon dioxide, and solutions of this kind constitute the *chalybeate mineral waters*.

Ferrous ammonium sulfate $((\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 6 \text{H}_2\text{O})$. When ammonium sulfate and ferrous sulfate are brought together in solution in molecular proportions, a double salt of the formula $(\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 6 \text{H}_2\text{O}$, known as *Mohr's salt*, separates on crystallization. This salt oxidizes less readily in the air than most other ferrous salts and is frequently employed in chemical analysis. All the sulfates which form vitriols yield similar double salts, not only with ammonium sulfate but also with the sulfates of potassium, rubidium, and cesium. The type of double salt represented by the general formula $2 \text{M}^+, \text{SO}_4^{--}; \text{M}^{++}, \text{SO}_4^{--}; 6 \text{H}_2\text{O}$ therefore includes many individuals, all of which are isomorphous.

Ferric compounds. In the ferric compounds iron acts as a trivalent metal; consequently the formulas of these compounds resemble those of the corresponding compounds of aluminum. All the simple ferric salts are largely hydrolyzed, their solutions acquiring the reddish-brown color of the hydroxide.

Ferric hydroxide $(\text{Fe}(\text{OH})_3)$. The only definitely proved crystalline hydroxide of iron known has the composition $\text{FeO} \cdot \text{OH}$ (or $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$). When a solution of a base is added to a solution of a ferric salt, a reddish-brown precipitate is formed, which for convenience is given the formula $\text{Fe}(\text{OH})_3$. Like the corresponding compound of aluminum (p. 603), it is a colloidal gel, and its composition varies with the exact conditions of its preparation. It may be regarded as an oxide with a varying degree of hydration. Iron rust is probably a mixture of such hydrated oxides.

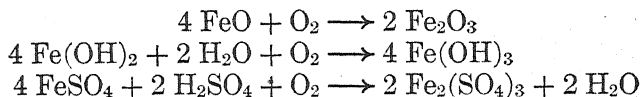
Ferric oxide (Fe_2O_3) . When the hydroxide is strongly heated, it forms the oxide, Fe_2O_3 , which is an insoluble red material occurring in nature in various forms of hematite, which range in color from red to black. The same compound is obtained by burning pyrite and, when carefully prepared, constitutes the pigment called *Venetian red*. Owing to its permanency, this is much used for painting structures that are exposed to the weather, such as bridges and railway cars. Ferric oxide is also found in nature, in combination with ferrous oxide, as the mineral *magnetite*, or *lodestone*, (Fe_3O_4) . This formula may be written $\text{FeO} \cdot \text{Fe}_2\text{O}_3$.

Ferric chloride (FeCl_3) . Ferric chloride is obtained in anhydrous form as a sublimate by heating iron in a current of chlorine. It is readily formed in solution by the usual methods, and crystallizes in a number of hydrated forms, of which the usual one has the formula $\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$. It is very soluble in water and to a less extent in

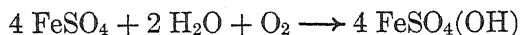
other solvents, such as alcohol and ether. Its solution in dilute alcohol constitutes the ordinary *tincture of iron* of the druggist.

Other soluble ferric salts. Of the other soluble ferric salts a few deserve special mention. The *sulfate* ($\text{Fe}_2(\text{SO}_4)_3$) can be obtained by the oxidation of green vitriol, as a white poorly crystallized substance. With the alkaline sulfates it forms a series of violet-colored alums, which, owing to their well-crystallized condition, are the ferric salts most frequently used. The most familiar one is the *ferric ammonium alum* ($\text{NH}_4\text{Fe}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$). The *nitrate* is deposited from concentrated solutions in well-formed, deliquescent crystals of the formula $\text{Fe}(\text{NO}_3)_3 \cdot 6 \text{H}_2\text{O}$, which have the same violet color as the alums. It is moderately soluble in dilute nitric acid, but readily forms supersaturated solutions. Potassium thiocyanate (KCNS) forms a complex thiocyanate when added to a ferric salt, which gives a blood-red color to the solution.

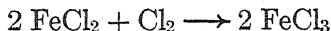
Oxidation of ferrous compounds. When exposed to the action of oxidizing agents, especially in the presence of water, ferrous compounds are readily oxidized to the corresponding ferric compounds:



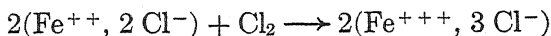
In moist air the oxidation produces a basic ferric sulfate, thus:



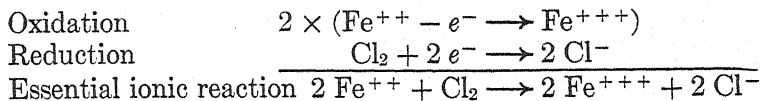
Oxidation and reduction of iron salts. The oxidation of iron from the *ferrous* (Fe^{++}) condition to its higher state of oxidation (*ferric*, Fe^{+++}), by an oxidizing agent such as chlorine, as shown in the equation



may also be represented in terms of ions and the charges which they carry,

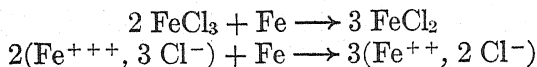


or in terms of ion-electron reactions:

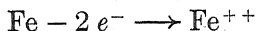


In reactions of this type the substance reduced (chlorine) is called the *oxidizing agent*, and the substance oxidized (ferrous ion) the *reducing agent*.

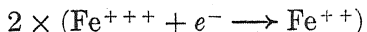
In like manner, the equation for the reduction of ferric iron by metallic iron may be written in ionic form to show the loss and gain of electrons:



Oxidation



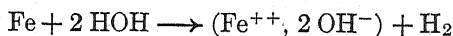
Reduction



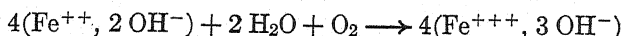
Essential ionic reaction $\text{Fe} + 2 \text{Fe}^{+++} \longrightarrow 3 \text{Fe}^{++}$

Electron arrangement in the iron atom. The atomic number of iron is 26, and consequently there are 26 electrons outside the nucleus. These are arranged in levels as follows: (2), (8), (14), (2), the 2 electrons in the last level being the ferrous valence electrons. The preceding valence level, (14), is incomplete, since if completed, the number would be (18). After the two usual valence electrons have been lost to form the ferrous ion (Fe^{++}), one more can be dislodged from the underlying (incomplete) level, leaving the arrangement $(2) + (8) + (13) = 23 = \text{Fe}^{+++}$. Considerations of this same kind explain the variable valence of the elements of the *A* families yet to be considered.

Reactions of rusting. The reactions in rusting are oxidation reactions and in a general way are thought to be as follows. Iron acts upon water thus:



The reaction would soon come to equilibrium were it not that the ferrous ions are oxidized to ferric ions by the oxygen dissolved in water:



Apparently rust consists of the porous hydroxide, $\text{Fe}(\text{OH})_3$, thus formed, combined with a variable amount of water.

Rusting is of enormous economic importance, since it is estimated that some \$3,000,000,000 is annually lost through the rusting of iron and steel. We may seek to diminish rusting (1) by searching for an alloy that is rust-resisting; (2) by depositing upon the surface of the iron a film of some plastic, like Bakelite (p. 532), or of some metal that is not acted upon by moist air (tinning, galvanizing); (3) by the use of various paints; (4) by heating the iron object and forming upon its surface a film of magnetic oxide (Fe_3O_4), which is not porous and protects the metal (Russia iron, gun barrels).

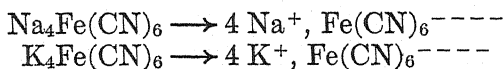
Complex compounds of iron. Iron forms a large number of complex compounds, of which the cyanides only will be described. Iron

forms no simple cyanides, but a very large number of complex cyanides are known, of which the ferrocyanide and ferricyanide of sodium and of potassium are the most important.

Sodium ferrocyanide ($\text{Na}_4\text{Fe}(\text{CN})_6$); **potassium ferrocyanide** ($\text{K}_4\text{Fe}(\text{CN})_6$). These two compounds are salts of the unstable ferrocyanic acid ($\text{H}_4\text{Fe}(\text{CN})_6$). They are prepared from by-products obtained in the manufacture of coke.

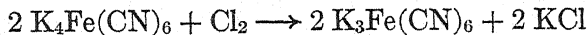
When coal is heated in the absence of air, small amounts of the carbon, nitrogen, and hydrogen present are evolved in the form of hydrogen cyanide. This is absorbed and converted into calcium ferrocyanide by means of calcium hydroxide and the spent iron oxide employed in the purification of the gas evolved in the coking of the coal. The calcium ferrocyanide so obtained is converted into sodium or potassium ferrocyanide by treatment with appropriate salts of sodium or potassium. The reactions involved in the complete process are quite complex.

Both sodium ferrocyanide and potassium ferrocyanide are yellow in color and are readily soluble in water. The latter compound is often called *yellow prussiate of potash*. The sodium salt crystallizes from water in the form of the hydrate $\text{Na}_4\text{Fe}(\text{CN})_6 \cdot 10 \text{H}_2\text{O}$, while the potassium salt crystallizes as the hydrate $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3 \text{H}_2\text{O}$. In solution they ionize as follows:



It is important to notice that the ions of iron are not present in sufficient concentration to give the ordinary reactions for iron.

Potassium ferricyanide ($\text{K}_3\text{Fe}(\text{CN})_6$). When potassium ferrocyanide in solution is treated with an oxidizing agent, a solution is obtained, from which crystallize garnet-red crystals of the composition $\text{K}_3\text{Fe}(\text{CN})_6$, known as *potassium ferricyanide*, or *red prussiate of potash*. With chlorine as the oxidizing agent the equation is as follows:

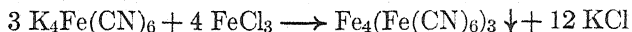


This compound in solution gives the ions 3K^+ and $\text{Fe}(\text{CN})_6^{---}$ but an inappreciable concentration of iron ions. Potassium ferricyanide is a salt of the unstable ferricyanic acid ($\text{H}_3\text{Fe}(\text{CN})_6$).

Other complex cyanides. Since the potassium in both ferrocyanide and ferricyanide acts as an ion, it is replaceable by other metals through double decomposition. Most of the ferrocyanides and ferricyanides so obtained are colloidal compounds insoluble in water and dilute acids. Copper ferrocyanide

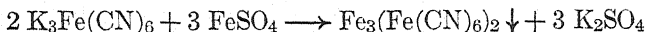
has already been mentioned in connection with its use as an osmotic membrane (p. 266). The compounds obtained by treating potassium ferrocyanide and potassium ferricyanide with simple ferrous and ferric salts are of especial interest.

With potassium ferrocyanide and ferric chloride the equation is



The complex product of this reaction is an indigo-blue precipitate, known as *ferric ferrocyanide*, or *Prussian blue*. It is used largely as a pigment.

With potassium ferricyanide and ferrous sulfate the equation is



The resulting complex is of much the same color as Prussian blue and is known as *ferrous ferricyanide*, or *Turnbull's blue*. The formation of these two precipitates affords a delicate method not only for detecting the presence of iron in the form of its salts but also for distinguishing between ferrous and ferric salts.

Blueprinting. When a ferric salt and potassium ferricyanide are brought together in solution, no precipitate forms, though the solution acquires a brownish color. On exposure to the sunlight the ferric salt undergoes a partial reduction to ferrous salt, and a blue precipitate forms. Advantage is taken of these facts in the process of blueprinting. A sensitive surface is prepared by soaking paper in a solution of potassium ferricyanide and a ferric salt (ferric ammonium citrate is generally used), and drying it in a dark place. When a black drawing on tracing cloth is placed upon such a sensitized paper and the two are exposed to the sunlight, the sensitized paper (except where it is protected by the black lines) turns a brownish color. It is then thoroughly washed with water to remove the soluble salts, the portions acted upon by the light turning blue, while the unaffected portions are left white. Both Prussian blue and Turnbull's blue are decomposed and thus decolorized by soluble bases, so that a solution of sodium hydroxide can be used as an ink for white lettering on a blueprint.

Ferric salts give a black precipitate with solutions of gallic acid (present in *nutgalls*) as well as with solutions of tannin (present in tea and in the barks of various trees). Advantage is taken of this reaction in the preparation of certain grades of black inks. Circular C 413, issued by the United States Bureau of Standards, gives interesting information concerning inks.

COBALT

Occurrence. Most minerals containing cobalt are strongly suggestive of the presence of a heavy metal, yet the older metallurgists were unable to smelt them and obtain this metal. For this reason they named the metal *kobold*, meaning "goblin," and this gave us

our name *cobalt*. The metal was finally obtained by the Swedish chemist Brandt in 1735. Cobalt usually occurs in combination with arsenic and sulfur, in complex minerals which also contain silver, iron, nickel, and copper. The simplest of these is *cobaltite* (CoAsS). Such minerals are found sparingly in many localities, but the richest known deposits are those located at Cobalt, Ontario, and in Africa. These are very rich in silver, and cobalt is worked up as a by-product, together with nickel and arsenic trioxide. In the Belgian Congo, cobalt is a by-product of copper-refining.

Metallurgy and properties. The metallurgy of the metal is very complicated, since it is difficult to separate cobalt and nickel. The pure metal is best prepared by the Goldschmidt process. It is a malleable, magnetic, silvery metal, which soon takes on a reddish tint upon exposure to the air. The metal is used chiefly in the form of alloys. *Cobalt chromium steels*, collectively known as *Stellite*, are used extensively in making high-speed cutting tools, since they retain their temper at high temperatures, and as important rust-resisting alloys. They are often modified by additions of tungsten, molybdenum, and nickel. An alloy called *Konel* contains cobalt, nickel, and ferrotitanium, and is harder than steel even when very hot. Metallic cobalt is used as a binding material for crystals of tungsten carbide in making the hard cutting material *Carboly* (see Chapter 39).

Oxides of cobalt. Cobaltous oxide, CoO , is the chief oxide of cobalt. In addition to this it forms two other oxides, Co_2O_3 and Co_3O_4 , corresponding to those of iron. Cobaltous oxide is a black powder used in making other cobalt compounds, blue glass, and blue decorations on china. When used as an ingredient in glasses, glazes, and enamels, it forms a blue silicate which has intense coloring properties. Sometimes the powdered blue glass called *smalt* is used instead of the oxide, and also as a pigment. In very small quantities it is used to correct the natural yellow color of clay, just as bluing whitens linen.

Salts of cobalt. Cobaltous oxide gives rise to a series of salts similar in formulas to the ferrous salts. In anhydrous form they are blue, but when hydrated they are usually cherry-red. The *simple* salts derived from cobaltic oxide, corresponding to the ferric salts, are very unstable, and few are well known. There are, however, a great many complex cobaltic salts. The hydrated *cobaltous nitrate* ($\text{Co}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$) and *cobaltous chloride* ($\text{CoCl}_2 \cdot 6 \text{H}_2\text{O}$) are the salts most frequently employed in the laboratory; both these salts are cherry-red in color. The *sulfide*, CoS , is formed as a black precipitate when a cobalt salt is treated with ammonium sulfide. It

dissolves slowly in dilute acids, but much more rapidly in concentrated ones. Some organic salts of cobalt are used as dryers in paints.

Potassium cobaltinitrite. When potassium nitrite and a salt of cobalt are brought into solution and treated with dilute acetic acid, a complicated reaction takes place in which the cobalt is oxidized to the trivalent state by the nitrous acid liberated in the reaction and an insoluble yellow salt is precipitated, $K_3Co(NO_2)_6$. It is known as potassium cobaltinitrite, and its formation is employed as a *test* both for cobalt and for potassium. Nickel does not form an insoluble compound under the above conditions, so that the reaction is used to separate nickel and cobalt from each other.

NICKEL

Occurrence and production. The early metallurgists were acquainted with certain minerals of high metallic luster, strongly resembling the ores of copper, but from which they could not extract that metal, and which they accordingly named *kupfernickel*, or false copper. The labors of Cronstedt and Bergman in Sweden, toward the close of the eighteenth century, resulted in the isolation of the new metal and its clear differentiation from cobalt.

Nickel is almost always associated with cobalt in nature. Like the latter element, it occurs in combination with sulfur and arsenic and is often associated with copper, silver, and iron. Most of its ores are very complex. It was formerly obtained, chiefly as a by-product, in the metallurgy of copper and silver. At present most of the world's supply comes from the Sudbury district in Ontario, Canada (Fig. 358). There the nickel occurs in the mineral *pyrrhotite* (a sulfide of iron) and is associated with chalcopyrite, the nickel-copper content being from 10 to 20 per cent. The Sudbury minerals contain small percentages of platinum, palladium, and iridium, and are a large source of these rare metals. The extraction of nickel from its ores is a complicated process.

Properties and uses. Nickel is a silvery metal capable of taking a very high polish. It is very hard, but is quite malleable. It can be welded on iron, and the two rolled into sheets for making various kitchen utensils. Like iron and cobalt, it is magnetic. It is not attacked by melted alkalis; hence nickel crucibles are often employed in the laboratory for alkali fusions. The nonoxidizing acids evolve hydrogen with nickel very slowly, but nitric acid dissolves it readily.

In many countries, including Switzerland and Canada, pure nickel is used for subsidiary coinage for a total of several billion



Galloway

FIG. 358. *Miners at Work in the Creighton Mine of the International Nickel Co., near Sudbury, Ontario*

coins. In the form of a fine powder it is a most effective catalyst in reactions in which hydrogen is added to an organic compound, as in the hydrogenation of oils (p. 525). It has been used extensively for electroplating on other metals, such as iron, brass, or copper, to prevent tarnishing. Chromium plating is largely replacing it, but a preliminary plating with nickel usually precedes plating with chromium. For nearly all other purposes it is used as an alloy metal.

Alloys of nickel. The older alloys were (1) for coinage, the United States using a five-cent piece containing 75 per cent copper and 25 per cent nickel, and (2) for German silver of about the same nickel content. For about fifteen years before the war of 1914-1918 nearly all the nickel produced went into armor plate, gun castings, and all sorts of ordnance equipment. More recently many new uses for nickel as an alloy metal have been developed. The nickel alloys, a great many of which have special trade names, may be classified as follows:

1. Low-nickel steel and cast iron, from $1\frac{1}{2}$ to 5 per cent nickel, for structural purposes, castings, and machinery parts.
2. Ferronickel alloys, from 35 to 80 per cent nickel, for electrical and magnetic uses.

3. Nickel-chromium-iron structural steel, from $1\frac{1}{2}$ to 5 per cent nickel, for automobiles and heavy machinery.

4. Noncorrosive (stainless) steel, containing chromium together with from 7 to 35 per cent nickel.

5. Nonferrous alloys, of which some four hundred are listed, the best-known being *monel metal*. This alloy consists approximately of 70 per cent nickel, 28 per cent copper, and 2 per cent iron. It is produced directly from the copper-nickel ores without separating the metals, and varies somewhat in composition. It is a silvery, malleable metal much used for sinks, dairy equipment, soda fountains, and for many purposes where cleanliness and resistance to mild corrosion are imperative.

Oxides of nickel. Nickel forms three well-known oxides, of the formulas NiO , Ni_2O_3 , and Ni_3O_4 , corresponding to those of iron and cobalt. Of these, *nickelous oxide* (NiO) alone gives rise to a series of simple salts, corresponding to the ferrous salts. When anhydrous, these are usually yellow, and when hydrated, some shade of deep green. Only a few of these require description.

Salts of nickel. *Nickel sulfide* (NiS), as prepared by precipitation, is a black amorphous powder, insoluble in water and dilute acids but easily soluble in more concentrated acids. *Nickel chloride* ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$), *nickel nitrate* ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), and *nickel sulfate* ($\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$) are the most familiar simple salts of this metal. The sulfate also forms crystals of the composition $(\text{NH}_4)_2\text{SO}_4 \cdot \text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, corresponding to Mohr's salt. It is the salt of nickel employed as the electrolyte in nickel plating, a piece of pure nickel being used as the anode and the object to be plated as the cathode. There are many complex salts of nickel.

Nickel carbonyl ($\text{Ni}(\text{CO})_4$). When carbon monoxide is passed over metallic nickel at a temperature between 30° and 50° , the two unite to form a compound of the formula $\text{Ni}(\text{CO})_4$, known as nickel carbonyl. It is a colorless liquid, boiling at 43.2° , and freezing at -25° to colorless, needle-shaped crystals. When the vapor of the compound is passed through a tube heated to above 100° , the compound dissociates into the metal and carbon monoxide. Advantage is taken of this reaction in the Mond process for purifying nickel.

Carbonyls of the other metals. Cobalt forms two carbonyls, $\text{Co}_2(\text{CO})_8$ and $\text{Co}_4(\text{CO})_{12}$, but both of these are solids and are formed only under pressure. Iron forms three, $\text{Fe}(\text{CO})_5$, $\text{Fe}_2(\text{CO})_9$, and $\text{Fe}_3(\text{CO})_{12}$. Of these the pentacarbonyl is a yellow liquid, freezing at -21° and boiling at 103° . When heated, iron carbonyls decompose like the nickel compound, and very pure iron can be obtained in this way.

Questions

1. (a) What are the functions of a blast furnace? (b) Describe in detail the blast-furnace process. (c) To what major uses are two products of the blast furnace put?
2. If you were operating a blast furnace, should you prefer to have the ore, coke, and limestone furnished to you in finely ground form, or in large lumps, or in pieces of medium size? Explain.
3. (a) Can steel of identical composition be made by the Bessemer and the open-hearth process? (b) Would there normally be any difference between the two products?
4. Distinguish (a) between steel and pig iron; (b) between steel and wrought iron.
5. What is the significance of the words *acid* and *basic* in the terms *acid Bessemer* and *basic open hearth*?
6. Describe the chemistry of the open-hearth steelmaking process.
7. How could one prepare ferrous chloride without the use of hydrochloric acid or metallic iron?
8. Chalybeate springs always have a rusty deposit of ferric hydroxide. Write ionic equations to account for this.
9. In the electrolysis of ferric nitrate the salt is reduced to ferrous nitrate at the cathode. Write the ionic equation.
10. Compare the physical properties and chemical conduct of iron, nickel, and cobalt.

Problems

1. If we assume that 50 per cent of the coke used in a blast furnace is consumed as fuel and 50 per cent as a reducing agent, and if hematite is used as ore, will it be more economical to locate the blast furnace at the coal mine or at the ore mine?
2. If you wished to prepare a ton of steel containing 5 per cent of tungsten, how much ferrotungsten containing 80 per cent tungsten would be required?
3. What weight of sulfuric acid of density 1.84 and containing 98 per cent of hydrogen sulfate will be required (in addition to an oxidizing agent) to convert 1 kg of ferrous sulfate into ferric sulfate?
4. What weight of hydrogen chloride can be obtained by the reduction of 1 kg of ferric chloride to ferrous chloride by nascent hydrogen?
5. Nine hundred grams of ferric chloride in solution was converted into ferrous chloride by the reducing action of iron. How much ferrous chloride was obtained?

6. Which contains the greater percentage of iron: $\text{Na}_4\text{Fe}(\text{CN})_6 \cdot 10 \text{H}_2\text{O}$ or $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3 \text{H}_2\text{O}$?

7. Nitric acid oxidizes iron to ferric nitrate. What volume of nitric acid of density 1.4 will be required to prepare 1 kg of crystallized ferric nitrate? (Assume that nitric acid acts on iron as on zinc.)

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Inks, Circular C 413, issued by the Bureau of Standards, can be obtained from the Superintendent of Documents, Washington, D.C. (price 10 cents).

CHAPTER 36

Three Inactive Metals and Their Compounds

NAME AND SYMBOL	ATOMIC WEIGHT	ATOMIC NUMBER	DENSITY	MELTING POINT	ELECTRONS IN SHELLS
Copper (Cu) .	63.57	29	8.92	1083°	2:8:18:1
Silver (Ag) . .	107.88	47	10.5	960.5°	2:8:18:18:1
Mercury (Hg) .	200.61	80	13.546	-38.87°	2:8:18:32:18:2

General. Although these three elements are not all in one periodic family (copper and silver belonging to one family and mercury to another), they have much in common, and it is convenient to describe them together. With the exception of antimony and bismuth they are the first metals we have met that are below hydrogen in the electromotive series and do not liberate hydrogen from acids or water. Unlike the metals already described, they sometimes are found free in nature. In the main, they occur as sulfide minerals, and their metallurgy is different from that of the metals we have been considering. They can all act as univalent metals in their salts, though bivalent salts of copper and mercury are the more usual ones.

History. Copper was probably the first metal to come into any considerable use. This is explained by its native occurrence in large pieces and by the ease with which its oxygen compounds are reduced. Well-fashioned copper articles have been found that are at least six thousand years old. The metal owes its name (from the Latin word *cuprum*) to the fact that the Romans obtained it from the island of Cyprus.

Silver, the *argentum* (white metal) of the Romans, appears in history later than copper and was prized along with gold as a precious metal free from corrosion. The alchemists gave it the symbol of the moon (*luna*), and we still have such names as lunar caustic (silver nitrate).

Mercury, or *quicksilver* (live, or running, silver) did not come into prominence before the beginning of the Christian Era. It played an important part in the alchemy of the Middle Ages.

Occurrence of the metals. While all these metals have been found free in nature, copper is the most noteworthy in this respect; and deposits of approximate purity are mined in the northern peninsula

of Michigan. Copper is also found as oxide, carbonate, and silicate, and silver as chloride (horn silver). However, the ores of all three metals are largely sulfides, very often in combination with sulfides of other metals. Examples of the most profitable of these various ores (aside from native copper) will be found in the following table :

Chief Ores of Copper, Silver, and Mercury

Chalcocite . . . Cu_2S	Malachite . $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$	Proustite . . Ag_3AsS_3
Chalcopyrite . CuFeS_2	Argentite . Ag_2S	Pyrargyrite . Ag_3SbS_3
Cuprite . . . Cu_2O	Horn silver . AgCl	Cinnabar . . HgS

Many ores of these metals are of very low grade, often less than 1 per cent, and are concentrated before smelting, usually by flotation.

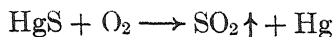
Production of the metals. Nearly all countries produce some copper. Chile probably has the largest single deposit yet discovered ; but the United States produces over a quarter, and North America nearly half, of the world's normal production, which totals about 2,000,000 tons annually. The chief copper states are Alaska, Montana, Michigan, Utah, Nevada, and New Mexico.

In addition to getting silver from the ores named in the table, some silver is obtained from native silver found in flakes or granules in certain rock formations, and much more from the sulfides of such metals as lead, copper, and nickel. Silver sulfide occurs in small percentages as a solid solution in these sulfides, and the silver is obtained as a by-product in the refining of these metals. The New World (North and South America) produces about 80 per cent of the world's output of silver, which totals some 17,000,000 pounds annually. Mexico produces more silver than any other one country ; the United States, somewhat less than Mexico ; and Canada, South America, Australia, and other countries make their contributions. In the United States, Idaho, Utah, Colorado, Arizona, Montana, and Nevada are the chief silver states.

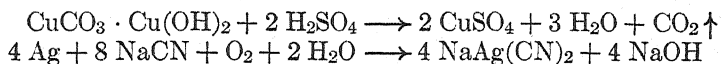
Mercury is found almost exclusively as cinnabar, together with some free metal in cinnabar mines. Spain and Italy have long been the great mercury-producing countries ; Mexico, California, and Oregon contribute much smaller quantities. The annual production has suffered much because of war conditions, but is normally about 5000 tons.

Metallurgy. These three metals introduce us to the general problem of the metallurgy of the sulfide minerals. The methods here employed differ from those based on electrolysis or the carbon reduc-

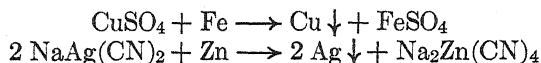
tion of the oxide. Broadly speaking, the problem may be approached in two ways: (1) leaching methods (hydrometallurgy) or (2) furnace methods (smelting, or pyrometallurgy). Mercury is unique in the simplicity of its metallurgy. Because of the ready decomposition of mercury compounds and the volatility of the metal, it is necessary only to roast the sulfide in a current of air and condense the mercury vapors:



Hydrometallurgy. This method is particularly adapted to oxide and carbonate ores of copper and to silver chloride. The metals or their compounds are readily dissolved from the finely crushed ore-bearing rock by suitable reagents, such as aqueous ammonia and dilute sulfuric acid, in the case of copper, or thiosulfate and cyanide solutions, in the case of silver:



Sulfide ores are sometimes roasted and then leached. For example, on roasting, silver sulfide is converted into silver sulfate, which is soluble in water. From these leaching solutions the copper or silver may be obtained by electrolysis or by precipitation with another metal (copper by iron, silver by copper or zinc):



Pyrometallurgy. In order to obtain a metal by smelting, the ore is concentrated, usually by flotation, and subjected to reactions in a melted condition.

1. **Copper.** In the case of copper, smelting is the more important of the two methods. The ore (usually in the form of sulfides, mixed or combined with other metallic sulfides, especially iron, as well as with small amounts of gold and silver) is heated with an appropriate flux in a blast furnace or reverberatory furnace. The sulfides of copper and iron melt, and the resulting liquid (known as *matte*) is separated from the slag and is poured into specially designed Bessemer converters. Any gold and silver present in the original ore is in solution in the liquid matte. Air is forced through the converter, and silica is then added. A certain percentage of the sulfides is changed into oxides by the process. The iron oxide combines with the silica, forming a slag that can be poured off, while the copper oxide reacts with some unchanged copper sulfide, as follows:



The resulting copper, which contains any gold or silver present in the ore, when cast in molds, is known as *blister copper*. This generally contains less than 3 per cent of impurities.

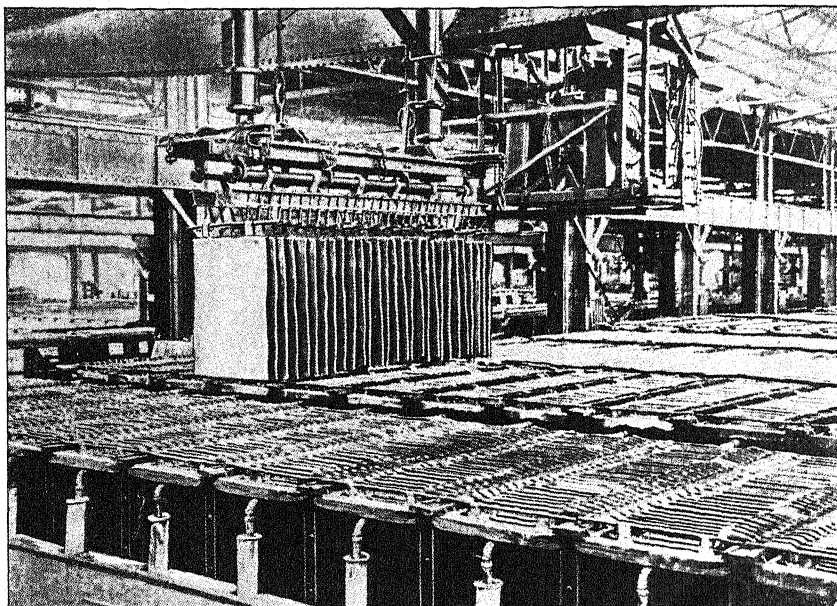


FIG. 359. *View in an Electrolytic Copper Refinery: Withdrawing the Pure Copper Cathodes from the Cells*

2. Silver. In furnace smelting, the silver ores are mixed with lead ores (if they are not already rich enough in lead), and the two metals are obtained as an alloy. The separation will be described in the following chapter.

Refining. For most purposes, the metals obtained in the metallurgical processes are refined not only to remove objectionable impurities but also to recover values in the precious metals which are present in the ores.

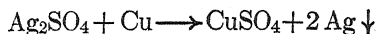
Copper. For refining, the liquid metal from the converter is charged onto the hearth of a reverberatory refining furnace resembling an open-hearth steel furnace. The impurities are oxidized and pass into a slag, but the gold and silver are not affected. The purified copper is then cast into anode plates weighing as much as 300 lb each. These are suspended in an electrolyte of copper sulfate and free sulfuric acid, and the anode copper is deposited upon a cathode of pure sheet copper (Fig. 359). The gold and silver collect in the mud at the bottom of the electrolytic cells, and this is worked over to obtain the precious metals.

Silver. There are a number of methods by which silver is refined, two of which may be mentioned:

1. Cupellation and parting with sulfuric acid. In this process the metal, alloyed with a large excess of lead, is heated on an open hearth in a strong

current of air. The various metallic impurities (excepting gold) are in this way largely converted into oxides and swept off as *dross*, leaving the silver alloyed with small percentages of gold, copper, and iron. The silver is then cast into ingots which are known as *doré* bars, since they contain gold.

In order to recover the gold, the alloy is treated with hot concentrated sulfuric acid, which converts all the metals, except the gold, into sulfates. When water is added to the resulting mixture, the sulfates of copper, silver, and iron pass into solution, while the gold (together with other unattacked substances) settles as a mud, from which the gold is subsequently recovered. To separate the silver from the solution of the sulfates, clean copper plates are suspended in the latter. The copper displaces the silver, which is deposited in crystalline form:



The copper sulfate obtained as a by-product in this process furnishes much of the blue vitriol of commerce.

2. Electrolytic refining. Electrolysis of the impure silver is now carried out extensively in a manner very similar to the electrolysis of copper. The electrolyte used is a solution of silver nitrate in nitric acid. The silver is deposited as crystals, which are mechanically brushed off the cathode, collected, and melted into bars.

Mercury. Solid materials that form a scum on the surface of mercury can be removed by filtration through soft leather. Dissolved metals (apart from gold) are oxidized to water-soluble compounds by flowing the mercury in a fine stream through a dilute solution of ferric chloride or nitric acid contained in a tall vertical tube.

More perfect purification is attained by slow distillation in a partial vacuum, with a very small stream of air drawn through the apparatus during distillation, as shown in Fig. 360.

Properties. Copper, silver, and mercury are all heavy metals. Mercury is the only familiar metal which is liquid at ordinary temperatures, and copper shares with gold the distinction of having color. Copper and silver are rather soft and are very ductile, malle-

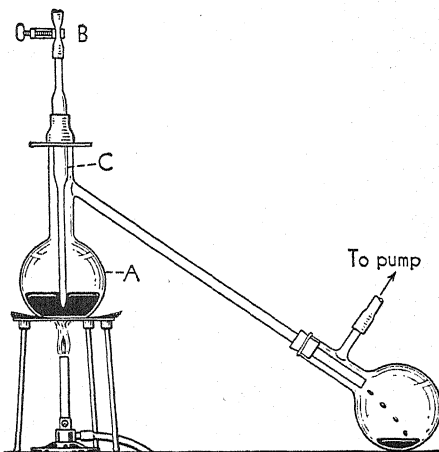


FIG. 360. Purification of Mercury

Mercury is purified by distillation from the flask A. The apparatus is partially evacuated by the pump, while a very small current of air is admitted at B and through the tube C (method of Hulett)

able, and flexible, yet tough and fairly strong. Silver surpasses all other metals as a conductor of heat and electricity, with copper a close second. Mercury is a moderately good conductor of electricity. All these metals alloy readily with other heavy metals; alloys of mercury are called *amalgams*.

Uses. Copper, silver, and mercury find extensive and varied uses.

Copper. About one fourth of all the copper produced is used for electrical purposes. Such copper must be exceedingly pure, since even minute quantities of impurities, especially arsenic, greatly diminish the electrical conductivity of the metal. The copper wire in telephone service alone would reach farther than the distance from the earth to the sun. Less pure copper has a wide use as a noncorrosive metal for roofing, for outside trim, for coppering the bottoms of ships, and for a wide range of factory and domestic utensils; it is also used for electrotyping.

A second very great use of copper is in the making of alloys. More than a thousand varieties of these alloys are recognized commercially, and the more familiar names, such as *brass* and *bronze*, now indicate merely the *type* of the alloy, since their composition is subject to wide variation. Some alloys, however, have rather definite compositions. Examples of each are given in the table on the opposite page.

Silver. Silver has long been used for coinage, jewelry, and tableware. For these purposes a small quantity of copper — from 7.5 per cent to 10 per cent — is melted with silver to give it hardness (sterling silver). The use of this metal is greatly restricted by its fixed coinage value, which takes it more or less out of the industrial field. Otherwise it would find more widespread uses in electroplating and in the preparation of special alloys. Silver steels have certain very desirable properties, and alloys with nickel or beryllium are useful as high-speed bearings.

From ammoniacal solutions, silver is slowly precipitated on the sides of the containing vessel by such mild reducing agents as certain sugars and other organic compounds. When deposited on glass, the tightly adhering film of silver forms a mirror. Because of the low reactivity of silver, mirrors may be used for long periods of time without deterioration. The silvered surface of a mirror in a reflecting telescope does tarnish in time, and this necessitates occasional resilvering. Recently such mirrors have been coated with aluminum, which retains its full reflecting luster much better than silver and reflects more ultraviolet light.

Mercury. The various properties of mercury give it great value for scientific purposes, as in manipulating gases, constructing ther-

Some Alloys of Copper

Variable Copper Alloys

[The elements other than copper are given in the order of their percentages.]

CLASS	COMPONENTS	CLASS	COMPONENTS
Simple brasses . . .	Cu, Zn	Ordinary bronze	Cu, Sn
Leaded brasses . . .	Cu, Zn, Pb	Phosphor bronze	Cu, Sn, P
Tin brasses . . .	Cu, Zn, Sn	Zinc bronze . . .	Cu, Sn, Zn, (P)
Leaded tin brasses .	Cu, Zn, Sn, Pb	Leaded zinc bronze	Cu, Sn, Zn, Pb
High-tensile brasses .	{ Cu, Zn, Al Cu, Zn, Fe	Lead bronze . . .	{ Cu, Sn, Pb, (Zn) Cu, Pb, Sn, (Zn)
Manganese brasses .	{ Cu, Zn, Mn Cu, Mn, Zn	Special bronze . .	Cu, Sn, X
Nickel silver (German silver)	{ Cu, Ni, Zn Cu, Zn, Ni	(X = any metal)	
Beryllium copper . .	Cu, Be	Aluminum bronze	{ Cu, Al Cu, Al, (Fe, Mg Mn, Ni, Pb, Si)

Constant Copper Alloys

NAME	PERCENTAGE COMPOSITION
18-carat gold	Gold 75%; copper, silver
14-carat gold	Gold 58%; copper, silver
Gold coin	Gold 90%; copper 10%
Silver coin	Silver 90%; copper 10%
Nickel coin	Copper 75%; nickel 25%
Sterling silver	Silver 92.5%; copper 7.5%

mometers and barometers, making electrical contacts where rigid wires are troublesome, and many similar applications. The readiness with which it dissolves gold and silver has at times led to its extensive use in obtaining these metals from their ores. Its relatively high boiling point (356.9°) has led to its use in high-temperature boilers instead of water. A single power plant of seven mercury boilers has been installed to use 270,000 lb of mercury — nearly 90 per cent of the average annual consumption of the metal in the United States.

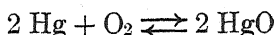
When cold, mercury vapor does not conduct the electric current. An arc is easily started in a tube containing the *heated* vapor, and a peculiar light fills the tube, rich in green and ultraviolet rays. Such a tube is called a Cooper-Hewitt lamp. Its soft, diffused light is well adapted to night work in drafting rooms and factories and is effective in street signs. If one electrode in such a tube is iron and the other mercury, the vapor will conduct the current in one direction only.

This mercury vapor lamp can be used to convert alternating currents into direct currents. Such a lamp is called a *rectifier*.

Fluorescent lamps. The "fluorescent lamp," which is rapidly coming into use, differs from the Cooper-Hewitt lamp in that the inside surface of the tube is coated with compounds, chiefly the tungstates and silicates of certain metals. At rest, the tube contains a drop of mercury, and some argon to facilitate starting. In action, the coating fluoresces and produces a light of superior quality.

Chemical conduct. Hydrochloric and dilute sulfuric acids and even melted alkalis are almost without action on copper, silver, and mercury, but nitric and hot concentrated sulfuric acids (oxidizing acids) readily dissolve them. In the presence of air most acids slowly act upon these metals. Even carbon dioxide and sulfur dioxide in moist air gradually cover the surface of copper with a greenish coating of a basic carbonate or basic sulfate.

When heated in air, copper is readily oxidized to the black oxide, CuO. Mercury slowly combines with oxygen at temperatures (300°) below its boiling point, but the action is easily reversed at higher temperatures:



It was by this reaction that Priestley discovered oxygen (p. 85). Silver combines with oxygen only under pressure, although it reacts more readily with ozone. While these elements do not combine directly with hydrogen, carbon, nitrogen, or silicon, they have a greater tendency to combine with sulfur and the halogen elements than with oxygen. The halogens attack silver slowly and only superficially, since impervious halides are formed which prevent further action. The blackening of silverware (formation of sulfide) by sulfur or sulfur compounds (such as those in eggs) is a familiar observation.

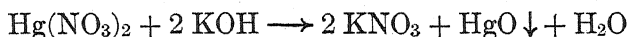
Compounds of the metals. Each of the three metals forms the long series of compounds we should expect to find with every metal. With silver there is but one such series (univalent), called simply silver compounds, such as silver chloride, AgCl. Copper and mercury have two series. As univalent metals they form such compounds as CuCl, cuprous chloride, and Hg₂Cl₂, mercurous chloride. As bivalent metals their chlorides are cupric chloride, CuCl₂, and mercuric chloride, HgCl₂. These two series pass the one into the other by reactions of oxidation or reduction, as in the case of ferrous and ferric compounds. All compounds of this group of metals are more or less poisonous, some very much so.

SIMPLE BINARY COMPOUNDS OF COPPER, SILVER, AND MERCURY

The binary compounds of copper, silver, and mercury are chiefly the oxides, sulfides, and halides. For convenience the hydroxides corresponding to the oxides are included with this group of compounds.

The oxides. Cupric oxide, CuO , and mercuric oxide, HgO , are the most familiar oxides of the group. They are sometimes made by decomposing such oxygen compounds as the nitrates or carbonates. Cupric oxide is a black powder and is easily reduced. When organic compounds are mixed with cupric oxide and heated, their carbon is oxidized to carbon dioxide. With the necessary apparatus, the carbon dioxide may be collected and weighed; this procedure permits the quantitative analysis for carbon.

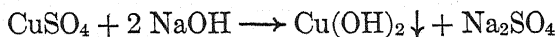
Mercuric oxide is prepared as a bright-red crystalline powder by the careful heating of mercuric nitrate. It is also obtained as a yellow precipitate when a cold solution of a soluble base is poured into a solution of a mercuric salt:



The yellow oxide changes into the red at a higher temperature.

Cuprous oxide, Cu_2O , is found in nature as ruby copper, or cuprite. It is precipitated as a copper-colored powder when an alkaline solution of a copper compound is warmed with a mild reducing agent, such as glucose. One such solution is called Fehling solution and is used as a test for certain sugars. Mercurous oxide, Hg_2O , and silver oxide, Ag_2O , are exceedingly unstable bodies that easily decompose into oxygen and the free metals.

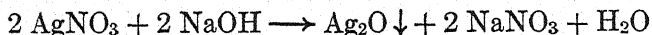
The hydroxides. The only well-defined hydroxide of this group is cupric hydroxide, $\text{Cu}(\text{OH})_2$. It is formed as a pale-bluish white colloidal gel when a *cold* solution of a cupric salt is treated with sodium hydroxide:



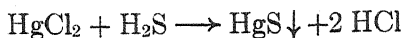
If the hydroxide in suspension is heated, it decomposes into the oxide and water:



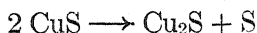
All the other hydroxides that might be expected in this group of metals (in both valences) are so unstable that they *spontaneously* decompose into oxides, and we do not have a hydroxide of silver or mercury that can be isolated:



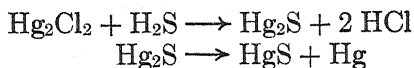
The sulfides. Cuprous sulfide, Cu_2S (chalcocite), and silver sulfide, Ag_2S (argentite), occur in nature as metallic-looking minerals of great value as ores; and mercuric sulfide, HgS (cinnabar), is the bright red ore of mercury. All the sulfides of this group of metals are highly insoluble in water and in dilute acids, and, as produced by precipitation, they are all black in color:



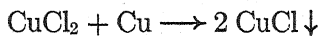
They are important compounds in chemical analysis. Cuprous sulfide can be made in the laboratory by heating cupric sulfide, preferably in a current of hydrogen:



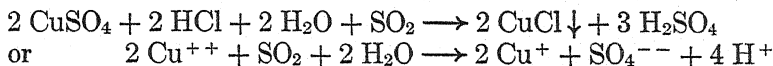
Neither cuprous sulfide nor mercurous sulfide is formed by precipitation, for reactions by which we might expect to prepare them always lead to cupric and mercuric sulfides by spontaneous oxidation-reduction:



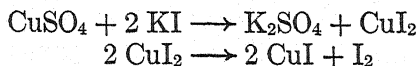
The halides. The halides in which the metals are univalent are all insoluble bodies (with the exception of the fluorides, which are all soluble). They are all colorless or nearly so, except that mercurous iodide is brown or deep yellow. Those of copper and mercury are all formed by the easy reduction of the bivalent halides. For example, cuprous chloride may be prepared by boiling a solution of cupric chloride in hydrochloric acid with metallic copper,



or by reducing a solution of a cupric salt dissolved in hydrochloric acid with sulfur dioxide:



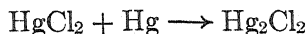
Cuprous iodide forms easily by spontaneous oxidation-reduction:



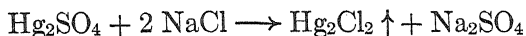
Cuprous chloride, dissolved in ammonium hydroxide (p. 671), combines with carbon monoxide to form a soluble compound; and such a solution is used in gas analysis to determine the volume of carbon monoxide in a gas.

Cupric chloride, $\text{CuCl}_2 \cdot 2 \text{H}_2\text{O}$, is a soluble salt that crystallizes in pearly scales or needles. It is easily made by dissolving copper oxide in hydrochloric acid.

Mercurous chloride, Hg_2Cl_2 , called *calomel* by the alchemists, can be made by heating a mixture of mercuric chloride and mercury:

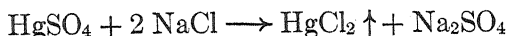


Usually it is made by heating mercurous sulfate with salt:



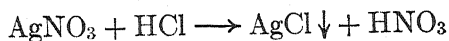
In either case the mercurous chloride leaves the mixture as a vapor and is condensed by being cooled (sublimation). It has important uses as a drug. In strong sunlight it tends to decompose into mercuric chloride and mercury, and for this reason it is kept in colored bottles.

Mercuric chloride, HgCl_2 , called *corrosive sublimate*, can be made in the usual way by dissolving mercuric oxide in hydrochloric acid, but practically it is obtained by heating a mixture of mercuric sulfate and salt:



The volatile chloride is condensed, as in the case of mercurous chloride. Prepared in this way mercuric chloride is a colorless crystalline compound soluble in water, in alcohol, and in other organic solvents. It is extremely poisonous and is used in surgery as an antiseptic. It combines directly with a great variety of substances, among others with albumin. This fact leads to the use of egg albumin as an antidote for poisoning by the compound, though no really effective antidote is known.

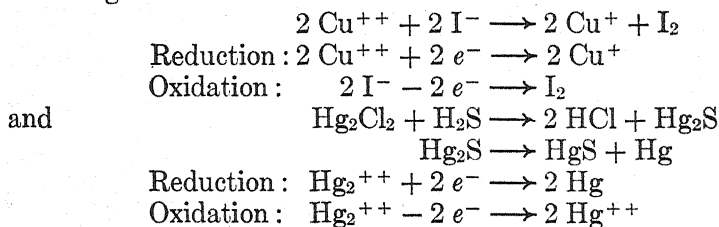
Silver chloride, *bromide*, and *iodide* are obtained by double decomposition as curdy precipitates by treating a soluble silver salt with either a soluble halide salt or the free acid:



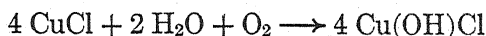
The chloride is white, the bromide slightly yellow, and the iodide decidedly so. All three of these salts are sensitive to light, and darken in color because of reduction of the silver ion. The extent of this reduction is proportional to the intensity of the light and the time of the exposure. It is upon facts such as these that the art of photography is based.

The mercurous ion. There has been much discussion about the true formula for mercurous compounds, particularly about whether the formula for mercurous chloride should be HgCl or Hg_2Cl_2 . X-ray and other studies indicate that the mercurous ion is a double atom of mercury with a double positive charge, namely $(\text{Hg}_2)^{++}$. The formula for the chloride should then be $(\text{Hg}_2)^{++}$, 2Cl^- or $\text{Cl}-\text{Hg}-\text{Hg}-\text{Cl}$ or Hg_2Cl_2 . For simplicity the formula is often written merely HgCl , though the double formula is the correct one.

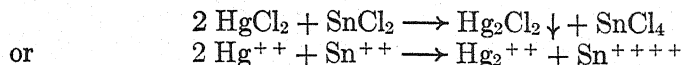
Reduction and oxidation reactions. Since copper and mercury form compounds in two stages of valence, we may expect many reactions in which cuprous or mercurous ions are oxidized to cupric or mercuric ions, or in which the latter ions are reduced to cuprous or mercurous ions. These changes take place with great ease, sometimes spontaneously by reactions of oxidation reduction, such as the following:



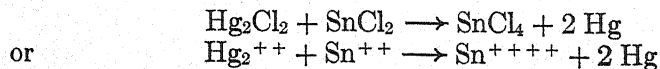
Even mild oxidizing or reducing agents often bring about changes in valence, as in the action of moist air on cuprous compounds by which they are oxidized into cupric compounds:



A reaction much used in analytical chemistry is the reduction of mercuric chloride to mercurous chloride by stannous chloride, SnCl_2 :



With an excess of stannous chloride, the mercurous chloride is in turn reduced to metallic mercury:



THE COPPER, MERCURY, AND SILVER SALTS OF
OXYGEN ACIDS

General. Mercury in both stages of valence forms simple salts with the stronger oxygen acids; but there are no bivalent silver salts and very few cuprous salts of these acids. Such salts, when formed at all, undergo spontaneous oxidation reduction in water solution:



There are, however, many complex salts containing cuprous copper. The various salts of oxygen acids can be prepared by the usual methods — by the action of acids on oxides, hydroxides, or carbonates; by precipitation of insoluble compounds; and by the action of oxidizing acids on the metals. It will not be necessary to describe more than a few of these salts in detail. Practically all the normal salts of silver and mercury are colorless or slightly yellow, except salts of colored acids, such as chromic acid or permanganic acid. Cupric salts are usually blue, both in solution and as solid crystals.

Silver salts. Of the three metals, silver acts as the strongest base. Silver oxide, shaken with water, turns red litmus blue; and silver salts are neutral in solution and are not hydrolyzed. A stable carbonate, Ag_2CO_3 , is precipitated by the action of sodium carbonate on a soluble silver salt, and moist silver oxide absorbs carbon dioxide from the air. Silver forms almost no hydrated salts.

Silver nitrate. The most used soluble salt of silver is the nitrate, AgNO_3 , which was called *lunar caustic* by the alchemists, for they gave silver the crescent symbol of the moon. Silver nitrate is extremely soluble in water, 100 g of solvent at 20° dissolving 215 g, and at 100°, 910 g. It crystallizes in colorless rhombic plates and melts undecomposed at 212°. It is often cast into sticks for use as a caustic in surgery, where its use depends upon the fact that it is a powerful oxidizing agent. It produces a black stain on the skin, which is a deposit of metallic silver. A similar stain is produced upon any other oxidizable material, such as cloth; and because of this fact, silver nitrate is used in the manufacture of indelible inks.

Other silver salts. Among important salts are the following:

Silver sulfate (Ag_2SO_4), sparingly soluble in water.

Silver acetate ($\text{AgC}_2\text{H}_3\text{O}_2$), crystallizing in shining needles.

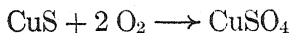
Silver cyanide (AgCN), a curdy white precipitate formed when a soluble cyanide is added to a silver salt.

Silver carbonate (Ag_2CO_3), a pale-yellow powder.

Silver chromate (Ag_2CrO_4), a brick-red amorphous solid.

Cupric salts. Bivalent copper acts as a somewhat weaker base than silver; and soluble cupric salts, even those of strong acids, are markedly hydrolyzed in water solution. The salts of the strong acids are normal salts, while with weak acids, such as carbonic acid, copper forms only basic salts.

Cupric sulfate (CuSO_4). The sulfate is the most important salt of copper. Under ordinary conditions it crystallizes from solution in blue triclinic crystals, often of very large size, having the composition $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ and known as *blue vitriol*, or *bluestone*. A number of other hydrates are known, all of which, when strongly heated, yield the anhydrous salt, which is white. In the industries copper sulfate is obtained in the refining of silver and by the oxidation of pyrite containing copper sulfide:



Prepared in these ways it contains a considerable percentage of ferrous sulfate as an impurity. It is used as a source of copper in the manufacture of other copper salts; as an electrolyte in copper refining, in electrotyping, and in batteries; and for the treatment of hoof diseases, particularly in sheep. *Fehling solution* (p. 665) contains copper sulfate dissolved in a solution of sodium potassium tartrate and sodium hydroxide. Many lower organisms, particularly those known as algae, are destroyed by even traces of soluble copper salts. Copper sulfate is sometimes added to the water supply of cities to kill the algae, whose growth gives an unpleasant taste and odor to the water.

Cupric carbonate. The normal carbonate of copper is not known, but there are a number of basic carbonates, the chief of which are $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ and $(\text{CuCO}_3)_2 \cdot \text{Cu}(\text{OH})_2$. Both of these occur in nature, the former as the green mineral *malachite*, and the latter as the blue mineral *azurite*.

Atmospheric corrosion of copper. It is well known that the copper of roofs, cornices, and architectural out-of-door ornaments of all kinds slowly turns green in color. This color material (patina) is usually a basic sulfate of copper which, through the years, slowly comes to the composition $\text{CuSO}_4 \cdot 3 \text{Cu}(\text{OH})_2$. Near the seashore, where traces of salt are present in the air, the ultimate composition of this covering is $\text{CuCl}_2 \cdot 3 \text{Cu}(\text{OH})_2$. Sometimes the basic carbonate, $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$, makes up a small part of the green patina.

Other cupric salts. Among the other cupric salts frequently used in the laboratory are the following, most of which form other hydrates in addition to those given:

Cupric nitrate ($\text{Cu}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$), blue deliquescent crystals
Cupric bromide (CuBr_2), brownish-purple crystals resembling iodine
Cupric acetate ($\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{H}_2\text{O}$), a blue easily crystallized salt

Salts of mercury. The oxides (or hydroxides) of mercury are still weaker bases than those of copper; and normal salts, even of strong acids, can be obtained only by crystallization from acid solutions. When dissolved in water, or even when the crystals are washed with water, these salts undergo partial hydrolysis and form basic salts. Some examples of both mercurous and mercuric salts are as follows:

Mercurous nitrate ($\text{Hg}_2(\text{NO}_3)_2$). This salt is formed when cold dilute nitric acid acts upon mercury. It is quite soluble and forms monoclinic needles of the hydrate $\text{Hg}_2(\text{NO}_3)_2 \cdot 2 \text{H}_2\text{O}$.

Mercurous sulfate (Hg_2SO_4). Mercurous sulfate is formed in a similar way by the action of sulfuric acid upon mercury. It is used in making standard electric cells.

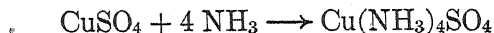
Mercuric nitrate ($\text{Hg}(\text{NO}_3)_2$). Mercuric nitrate crystallizes from dilute nitric acid in the form of a hydrate of the composition $\text{Hg}(\text{NO}_3)_2 \cdot 8 \text{H}_2\text{O}$.

Mercuric fulminate ($\text{Hg}(\text{OCN})_2$). Mercuric fulminate is prepared by the action of nitric acid upon mercury in the presence of alcohol. It is extremely explosive and is used in the manufacture of primers for cartridges.

SOME COMPLEX COMPOUNDS OF COPPER, SILVER, AND MERCURY

The three metals of this group form a great many complex compounds, and the ones formed by the action of ammonia or ammonium hydroxide and of soluble cyanides upon salts of these metals are of special interest.

Ammonia compounds of salts of copper and silver. When any soluble salt of copper is treated with aqueous ammonia, copper hydroxide, $\text{Cu}(\text{OH})_2$, is at first precipitated but at once dissolves in any excess of ammonia to form an intensely blue solution. From such a solution crystals of the same intense color can be obtained. From copper sulfate, thus treated, crystals of the composition $\text{Cu}(\text{NH}_3)_4\text{SO}_4 \cdot \text{H}_2\text{O}$ may be obtained:



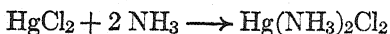
Copper is not precipitated from such a solution by many reagents that usually precipitate the copper ion as an insoluble compound. It has been shown that the copper forms a part of the complex cation $\text{Cu}(\text{NH}_3)_4^{++}$ in all these copper salts, whatever the anion may be.

Salts such as $\text{Cu}(\text{NH}_3)_4\text{SO}_4$ are called *ammoniates* because they are similar to hydrates in many ways. A large number of metals form such salts.

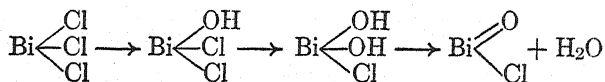
Silver salts dissolve in excess of ammonium hydroxide to form ammoniates with two molecules of ammonia, such as $\text{Ag}(\text{NH}_3)_2\text{Cl}$ and $\text{Ag}(\text{NH}_3)_2\text{NO}_3$. Silver chloride, insoluble in water, therefore dissolves in ammonium hydroxide.

Ammonia compounds of mercury. The action of ammonia on compounds of mercury in water solution is more complex than with salts of other metals, and this action (as well as reactions in liquid ammonia) has been studied most extensively by the American chemist Franklin. The reactions can be understood most readily by remembering that ammonia and water as solvents have many properties in common and that their reactions with salts are closely analogous. The compounds formed by the action of ammonia or ammonium hydroxide on compounds of mercury may be classified in three groups, as follows:

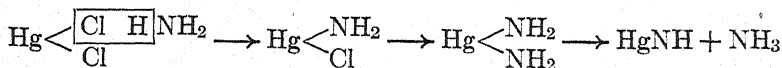
1. *Compounds analogous to hydrates (ammoniates).* A mercuric salt treated with excess of aqueous ammonia under proper conditions may form an ammoniate. For example:



2. *Compounds analogous to basic salts.* The hydrolysis of salts has already been explained (p. 372) and is well illustrated in the case of bismuth chloride, in which the following stages may be pictured as occurring:

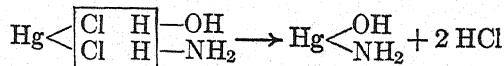


With mercuric salts there is a corresponding action, which Franklin has aptly named *ammonolysis*. With the chloride the stages are



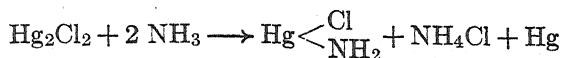
Compounds of this type, formed by ammonolysis and analogous to basic salts, are called *ammonobasic* salts.

3. *Mixed types.* When mercury salts are treated with *aqueous* ammonia, which may be regarded as a mixed solvent consisting of water and ammonia, *both hydrolysis and ammonolysis may occur*. In the case of the chloride this is represented by the equation



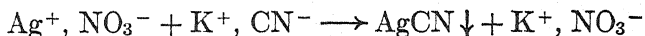
The product of this reaction is both *water-basic* and *ammonobasic*.

Reactions which can be referred to these types occur with most mercuric salts. With mercurous salts there is at the same time a decomposition which results in the formation of a mercuric derivative and free mercury, as is illustrated in the case of calomel:

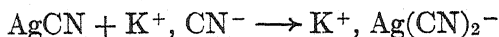


The ammonobasic mercuric chloride formed in this reaction is a white compound, but it appears to be jet-black, owing to the finely divided mercury precipitated at the same time. Many of these compounds were known long before their nature was understood, and their older names have little meaning.

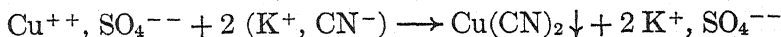
Cyanide compounds of copper, silver, and mercury. The simple cyanides of most of the metals other than the alkali metals are insoluble in water, and we should expect them to be precipitated by double decomposition with an alkali cyanide, such as potassium cyanide. With a silver salt we should expect the reaction



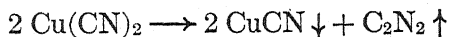
This reaction does take place, but the insoluble silver cyanide dissolves in excess of potassium cyanide to form the complex salt $\text{KAg}(\text{CN})_2$, in which the anion is $\text{Ag}(\text{CN})_2^-$:



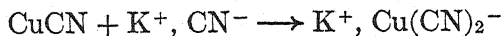
With copper salts a similar reaction takes place:



But the cupric cyanide spontaneously decomposes to cuprous cyanide and cyanogen:

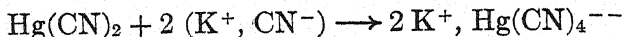


The insoluble cuprous cyanide then dissolves in excess of potassium cyanide:



It will be seen that *cupric* salts yield complex *cuprous* salts by treatment with soluble cyanides.

Mercuric cyanide, $\text{Hg}(\text{CN})_2$, is an unusual cyanide for one of a heavy metal, for it is soluble in water. Treated with a solution of potassium cyanide, it forms the double cyanide:



PHOTOGRAPHY

Silver and photography. Next in importance to the use of silver for coinage comes its use for sterling silver and then for photography (Fig. 361). Photographic plates and films annually absorb more than



FIG. 361. *Silver Ingots*

Six thousand pounds of silver — about half of a week's supply at the kodak factory

6,000,000 oz of silver, and much of this is permanently lost. The "movie" films made in 1940, if placed end to end, would encircle the earth about fifteen times.

The process of photography in its simplest form may be described briefly as follows :

1. **Preparation of the negative.** The plate used in the preparation of the negative is made by spreading a thin layer of gelatin, in which colloidal silver bromide is suspended (silver iodide is sometimes added also), over a glass plate or more often a nitrocellulose film and allowing it to dry. When the plate so prepared

is placed in a camera and the image of some object is focused upon it, the silver salt undergoes a complicated change which is proportional at each point to the intensity of the light falling upon it. In this way an image of the object photographed is produced upon the plate. This image, however, is invisible and is therefore called *latent*. It can be made visible by the process of *developing*.

To develop the image the exposed plate is immersed in a solution of some reducing agent called the *developer*. While the developer will *in time* reduce all the silver salt, it acts much more rapidly upon that which has been exposed to the light. The action is therefore continued only long enough to bring out the image. The reduced silver is deposited in the form of a black film which adheres closely to the plate.

The unchanged silver salt is now removed from the plate by dipping it in a solution of sodium thiosulfate (*hypo*, p. 585). The plate is then washed with water and dried. The plate so prepared is called the *negative* (Fig. 362) because it is a picture with the lights and directions exactly reversed.

2. **Preparation of the print.** The print is made on paper which is prepared in much the same way as the negative plate. The negative is placed upon this paper and exposed to the light in such a way that the light must

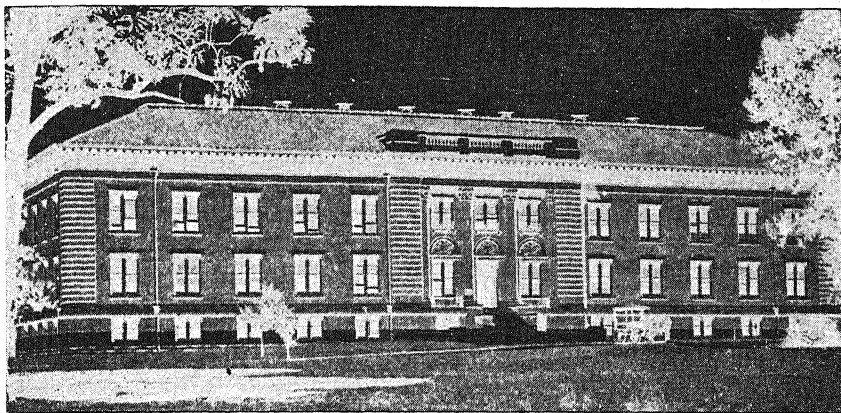


FIG. 362. *Photography: the Negative from Which the Positive Print Is Made*

pass through the negative before striking the paper. If the paper is coated with silver chloride, a visible image is produced, in which case a developer is not needed. *Proofs* are made in this way. In order to make them permanent the unchanged silver chloride must be dissolved off with sodium thiosulfate. If desired, the print may be *toned* by dipping it into a solution of salts of gold or of platinum, in which process the silver on the print passes into solution, gold or platinum replacing it. Since the darkest places on the negative cut off the most light, the lights of the print (Fig. 363) will be the reverse of those of the negative and will correspond to those of the object.

The light-sensitive silver halides are most affected by violet and ultra-violet light waves. Reagents have been found that are sensitive to the longer red waves. These are not so easily absorbed by water vapor in the air, and by them photographs can be taken even through clouds.

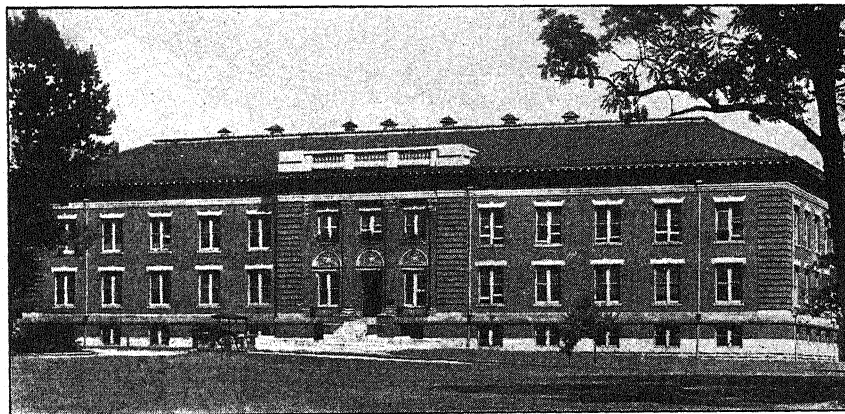


FIG. 363. *Photography: the Positive Print Made from the Negative*

Questions

1. Apart from copper, what other metals have a distinguishable color?
2. Apart from mercury, what other elements are liquid at ordinary temperatures?
3. Copper, silver, and gold are sometimes called the currency metals. Why?
4. Is it safe practice to use copper pipes for conveying drinking water? Explain.
5. Which cell will furnish the higher voltage, (a) one having electrodes of zinc and copper or (b) one having electrodes of zinc and silver? Explain.
6. All cuprous salts have a marked tendency to undergo spontaneous oxidation reduction according to the equation $2 \text{Cu}^+ \longrightarrow \text{Cu}^{++} + \text{Cu}$. Why, then, is it possible to prepare cuprous chloride by the reaction of metallic copper on cupric chloride?
7. Why not prepare silver chloride like mercurous chloride, that is, by heating silver sulfate with salt?
8. It is said that mercury was known twenty-five hundred years ago. Why should it have been known so long before other more abundant metals, such as zinc?
9. Silver oxide is easily prepared. Why is it not formed, together with lead oxide, in the cupellation process?
10. In parting silver from gold with sulfuric acid, silver is converted into silver sulfate. Write the equation.
11. Why does the addition of sodium carbonate to a solution containing compounds of copper sometimes cause a precipitate and sometimes not?

Problems

1. What weight of chalcopyrite will be required to furnish the copper for 100 kg of silver dollars?
2. What weight of 98 per cent sulfuric acid will be required to part the silver from the gold in 100 g of an alloy containing 80 per cent silver?
3. A man bought 500 g of calomel, but by mistake he was given corrosive sublimate. Being a chemist he transformed it into calomel. (a) How could he do it? (b) What weight of calomel did he obtain?
4. One gram of a silver dollar was dissolved in nitric acid, and the silver was precipitated as silver chloride. The precipitate weighed 1.1957 g. Was the dollar genuine?

5. A lot of old "movie" films were soaked in sodium thiosulfate, and the solution was diluted to 1 l. Five cubic centimeters of the solution was decomposed by hydrochloric acid, and the silver was collected and weighed as silver chloride. It weighed 2 g. How much silver could be recovered from the remainder of the solution?

Reading References

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HOWARD. "The Story of Copper," *Journal of Chemical Education*, Vol. VI, pp. 413-431.

MEES. "The Processes of Color Photography," a series of four articles printed in the *Journal of Chemical Education*, Vol. V, pp. 1385, 1577; Vol. VI, pp. 44-51, 286-291.

NEBLETTE, BREHM, and PRIEST. *Elementary Photography*.

SHEPPARD. "The Chemistry of Photography," a series of three articles printed in the *Journal of Chemical Education*, Vol. IV, pp. 298-312, 465-473, 749-757.

SULLIVAN. "Leaching Copper from Its Ores," *Journal of Chemical Education*, Vol. VIII, pp. 829-847.

WEEKS. *The Discovery of the Elements*. Read of the discovery of copper, silver, and mercury.

A series of six articles entitled "Chemistry for the Amateur Photographer" printed in the *Journal of Chemical Education*, Vol. VI, pp. 2002-2007, 2246-2252; Vol. VII, pp. 420-433, 882-890, 1154-1158, 1388-1399.

Consult the Minerals Yearbook for the production of copper, silver, and mercury.

Tin, Lead, and Related Metals; Paints and Varnishes

ELEMENT AND SYMBOL	ATOMIC WEIGHT	ATOMIC NUMBER	DENSITY	MELTING POINT	ELECTRONS IN SHELLS
Germanium (Ge)	72.60	32	5.36	958.5°	2:8:18:4
Tin (Sn) . . .	118.70	50	7.31	231.85°	2:8:18:18:4
Lead (Pb) . . .	207.21	82	11.34	327.5°	2:8:18:32:18:4
Thorium (Th) .	232.12	90	11.20	1845.°	2:8:18:32:18:8:4

Place in the periodic table. Germanium, tin, and lead constitute family *B*, Group IV, in the periodic table, while thorium is the end member of family *A* in the same group. The chapter will be devoted mainly to tin and lead, with very brief comment on the rare metals germanium and thorium.

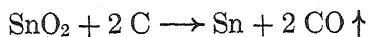
Historical introduction. Tin and lead are two of the six metals known to the ancient world, though neither metal is found in the free state in any appreciable extent. Objects of tin-bronze date back more than five thousand years. Tin was long confused with lead and was sometimes called white lead. The distinction between the two metals was first clearly indicated in the writings of Pliny in the first century A.D. Tin was later called *stannum*, whence the names *stannous* and *stannic* and the symbol Sn.

Articles made of lead have been found in ruins of great antiquity, and the metal was evidently in common use in very early times. The Romans called it *plumbum* (which gives us the symbol Pb) and used it for water pipes, much as we do today.

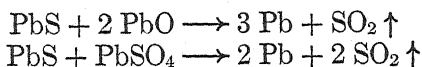
Occurrence. Tin is found chiefly as the oxide, SnO_2 , called tin-stone, or *cassiterite*, and this is the only metallurgical ore. Until the thirteenth century tin was apparently obtained from Cornwall (England), but at present the Malay States stand first in production, followed by Bolivia, the Dutch East Indies, and Siam. Tin is one of the few metals of industrial importance not found to any extent in the United States. The annual production of the United States is only about 150 tons; yet it uses from one third to one half of all the tin mined in the whole world.

In contrast to its small contribution of tin, the United States leads all other countries in the world's output of lead; and the chief mining states are Missouri, Idaho, and Utah. Australia and Mexico rank next to the United States. The minerals of most value to the metallurgist are *galenite* (galena), PbS , and to a less extent *cerussite* (PbCO_3) and *anglesite* (PbSO_4). The average price of lead is about 5 cents per pound, as compared with from 40 cents to 50 cents for tin. Next to iron, lead is our cheapest metal.

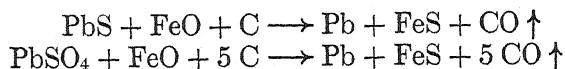
Metallurgy. The metallurgy of tin depends on an *oxide* reduction similar to that of iron; the metallurgy of lead is a *sulfide* reduction like that of copper. The chief impurities of tin oxide ores are sulfides of copper and iron, together with small percentages of arsenic. The ore is first concentrated (usually by flotation) and is then roasted in air to drive off all arsenic as volatile oxide and to convert the sulfides into soluble sulfates. The sulfates are washed out with water or dilute acids, a flux of limestone and silica is added to the ore, and the tin oxide is reduced by carbon:



The ores of lead are chiefly *sulfides*, usually associated with more or less silver sulfide and often a little gold; silver ores are often purposely added to silver-bearing lead ores and the two metals smelted together. When no silver is present, the ores are roasted in air in an open oven until they are partially oxidized to form a mixture of sulfide, sulfate, and oxide of lead. Access of air is then shut off and the temperature raised to bring about the following reactions:



Silver-bearing ores are worked at a higher temperature in a blast furnace the bottom of which consists of a large crucible-like structure made of firebrick. The roasted ore is charged into the furnace along with coke and a flux consisting of limestone and iron ore. The chief reactions that produce lead (and silver) are these:



The liquid lead, carrying the silver and gold in solution together with varying percentages of copper, antimony, bismuth, and arsenic, collects in the crucible and is tapped off.

Refining of lead. The lead from the blast furnace is *hard* because of the metals alloyed with it. It is refined (softened) by a number of methods, largely by the two following ones:

1. **The Parkes method.** The impure lead is heated just to its melting point and kept at this temperature for a time. Copper is but slightly soluble in lead at this temperature, and rises to the surface and is skimmed off. The lead is then heated to a higher temperature during a number of days for the air to oxidize the arsenic, antimony, and bismuth present. These oxides form a scum (*dross*) on the surface of the lead and are removed. The lead is then transferred to a huge kettle in which it is kept melted; then a small percentage of zinc is added, and the liquid metal is thoroughly stirred. Gold, silver, and copper are much more soluble in zinc than in lead, and zinc is little soluble in lead. As a result of these differences in solubility, as soon as the stirring ceases the zinc rises to the surface of the lead, together with the other metals dissolved in it. When the temperature is lowered, the zinc alloy forms a solid crust, which is removed; and the operation is repeated until all the precious metals have been extracted from the lead.

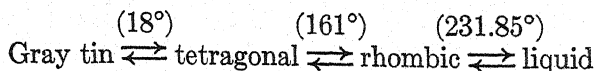
The zinc crusts are distilled from a retort, and the zinc is recovered to be used again. The residue contains the gold and silver. Some zinc remains in the lead, and this is removed either by oxidation or by converting it into the chloride by treatment with chlorine.

2. **The electrolytic process (Betts process).** In this process impure lead is used as the anode in a cell in which the electrolyte is fluosilicic acid and lead fluosilicate (PbSiF_6). Pure lead is deposited on the cathode, and the precious metals are recovered from the spent anode plates and the electrolytic muds.

In both these processes the silver is parted from the gold of the residues, as explained in connection with silver (p. 660).

Properties of the metals. As we ordinarily see it, tin is a silver-white metal, harder than lead and quite malleable. It is a low-melting metal and is slightly lighter than iron. Lead is a heavy, silvery metal and is the softest of the industrial heavy metals. It is malleable, has little strength, and is a moderately good conductor of electricity. It crystallizes in the isometric system.

It is of interest that tin occurs in three allotropic forms which pass the one into the other at definite transition temperatures:



The first of these transitions is especially interesting because it takes place at ordinary temperatures. Below 18° ordinary white tin (tetragonal) is in an unstable state and under some conditions changes

into the gray form ; at the same time it loses its metallic appearance and crumbles to a powder.

Tin plague. The transformation of white tin into the gray form is sometimes a serious matter (Fig. 364). It was first noticed in connection with the deterioration of some organ pipes made of tin, which developed holes and

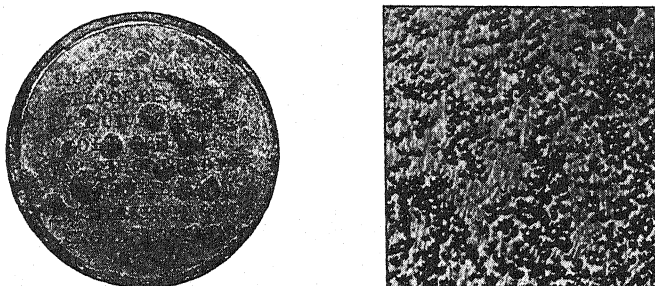


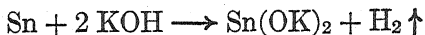
FIG. 364. *Tin Objects in a Museum, Showing the Transformation of White Tin into the Gray Form (Museum Tin Disease)*

then broke up completely. Later, ingots of tin stored in a Russian custom-house during a very cold winter were found to have crumbled to powder. When the transformation once starts, it continues to spread as long as the temperature is below 18° , and this uncontrollable spread has been called the tin plague, or museum disease, since it sometimes spreads over tin objects in a cold museum. The speed of the transformation is increased by contact with a solution of certain salts in which tin is slightly soluble.

Chemical conduct of the metals. In the electromotive series tin and lead are close together just above hydrogen, and we should expect them to have very similar chemical properties. Their similarity is somewhat disguised by the fact that many simple compounds of lead are insoluble and form protective coverings on the surface of the metal. Tin slowly reacts with both hydrochloric and dilute sulfuric acids, with evolution of hydrogen ; but lead quickly becomes covered with a protective film of lead chloride or sulfate. Tin is not perceptibly affected by air or water at ordinary temperatures, while a film of oxide forms on the surface of lead, changing its silvery luster to a dull blue-gray, and finally forms a thicker covering of white basic carbonate. Soft water containing dissolved oxygen acts on lead to form the somewhat soluble lead hydroxide, $\text{Pb}(\text{OH})_2$.

Weak nonoxidizing acids, such as acetic acid, act on lead more readily than on tin. Oxidizing acids, such as nitric acid or concentrated sulfuric acid, oxidize tin to an insoluble hydrate of the oxide

SnO_2 , while they act on lead as they do on copper (p. 388) to form lead nitrate or lead sulfate. Strong alkalies act on both metals as they do on zinc (p. 105). For example:



All compounds of lead are poisonous and tend to accumulate in the system, and all workers with the metal or its compounds must use precautions against lead poisoning.

Uses of the metals. The important uses of tin and lead as metals depend largely on their resistance to more than superficial corrosion and on their value in alloys.

More than one third of the tin imported into the United States is used in making tin plate by dipping sheet iron into melted tin (see galvanized iron, p. 598) or by electroplating the tin on the iron. The iron is strong and cheap, and the tin gives resistance to corrosion. The large uses of tin plate are for making tin cans, roofs, and cooking vessels. Tinned copper is sometimes used for this last purpose. Pure tin pipes of small size are used for conveying pure water in laboratories. Lead water pipes have long been used because they are flexible and easily installed. With any ordinary water the interior of the pipe quickly becomes covered with a protective coating of basic carbonate or sulfate. With rain water or other very soft water enough lead passes into solution as hydroxide to be a threat to health. Iron pipes have largely taken the place of lead ones. The condensing chambers of sulfuric acid plants are covered with sheet lead (p. 365) to resist corrosion by the dilute acid that collects in the chambers. Architectural devices, such as the mullions for holding glass in windows, are often of nearly pure lead.

The second great use of tin and lead is in making alloys. Many of these, such as bronze, bearing metals, low-melting metals, and some brasses, have been described in connection with copper and other metals. *Soft solder* and pewter are essentially alloys of tin and lead, though the latter usually contains some antimony to harden it. *Type metal* consists of the same three metals. Tin foil often contains some lead; it has been largely replaced by aluminum foil and cellophane. The greatest use of lead is for making storage batteries, and the supporting grid of the battery plates is a lead-antimony alloy. The sheathing for the protection of electric cables is either lead itself or an alloy of lead with variable percentages of calcium and barium. This alloy, called *Frary metal*, is made by electrolyzing a fused mixture of the chlorides of calcium and barium, with the use of a liquid lead cathode in which the depositing metals dissolve.

Shot is an alloy of lead and a very small percentage of arsenic. A great many bearing metals and antifriction metals contain lead as a component (p. 550).

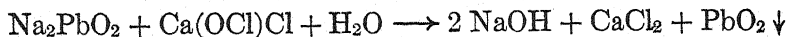
Rusting of tin plate. If the coating of tin on tin plate is scratched through to the iron, the iron will rust faster than if there were no tin covering. The two metals and the water constitute a battery much like the Daniell cell (p. 561), and in a battery the metal highest in the electromotive series is the one that is corroded. In the case of galvanized iron the zinc rusts first, and the iron resists rusting as long as any zinc is present.

Soldering and brazing. The use of solder in joining two metal surfaces depends upon (1) the low melting point of the solder and (2) the fact that it flows over *clean* metal surfaces and sticks to them on cooling. To secure clean surfaces free from oxide a suitable flux must be used which will either *dissolve* the oxide as fast as it forms or *reduce* it again to metal or float it away. The usual fluxes are zinc chloride, ammonium chloride, rosin, and stearin. In *brazing*, or *hard soldering*, the process is essentially the same, except that a low-melting brass is used instead of solder, and borax is used as a flux.

Compounds of tin and lead. In practically all their compounds tin and lead act either as bivalent or as quadrivalent elements. Acting as bivalent metals their compounds are designated as *stannous* and *plumbous*; as quadrivalent metals they form *stannic* and *plumbic* compounds. Lead is rarely quadrivalent, and the bivalent compounds are referred to merely as lead compounds.

The valence oxides. Stannous oxide, SnO , can be obtained as a black powder by heating stannous oxalate, SnC_2O_4 ; but it is rarely prepared. Lead oxide, PbO , called *litharge*, is made by heating lead in a current of air or by heating the carbonate. It is a by-product in cupeling silver-lead alloys (p. 660). In color it ranges from yellow or light brown to orange, depending on the way in which it is made. The light-brown form is called *massicot*. Its chief use is in making paints, glass, glazes, and other compounds of lead. Mixed with glycerin it forms a cement useful for joining glass and stone.

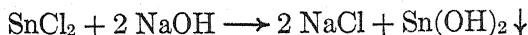
Tin dioxide, SnO_2 , is the chief mineral ore of tin. By burning tin in air or by treating it with nitric acid and heating the resulting hydrated oxide, it is obtained as a white powder. It is used in making opaque glass and enamels. Plumbic oxide, PbO_2 , usually called *lead dioxide*, is a dark-brown powder. It is obtained by the action of bleaching powder on sodium plumbite (Na_2PbO_2):



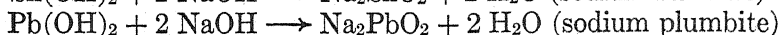
It forms a brown coating on the anode when solutions of lead salts are electrolyzed, and is the active material on the anodes of storage batteries (p. 564). It is a good oxidizing agent. For example, with hydrochloric acid it acts much like manganese dioxide and evolves chlorine:



The hydroxides. The hydroxides of tin and lead in both stages of valence are amphoteric in character. They form salts with both acids and bases. When stannous chloride or lead nitrate is treated with sodium hydroxide, the hydroxide of either metal is at first precipitated as a white amorphous gel. For example:



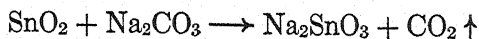
Excess of sodium hydroxide causes these precipitates to dissolve (as with zinc hydroxide) to form *sodium stannite* and *sodium plumbite*:



Sodium stannite hydrolyzes markedly in solution, and the stannous hydroxide so produced is a strong reducing agent. Sodium plumbite is used to desulfurize gasoline.

When a solution of stannic chloride (SnCl_4) is treated with ammonium hydroxide, a white colloidal gel is precipitated. Like the colloidal gel of silica and of most metallic hydroxides, no definite formula can be assigned to it beyond regarding it as a hydrated oxide, $\text{SnO}_2 \cdot x \text{H}_2\text{O}$. Treated with strong acids, it forms salts, such as the sulfate, $\text{Sn(SO}_4)_2$; and treated with sodium hydroxide, it dissolves to form the sodium salt of an acid assigned the formula H_2SnO_3 , called *metastannic acid*. A few salts are known derived from the acid H_4SnO_4 , called *orthostannic acid*. The compound formed by the action of nitric acid on tin has approximately the formula of *metastannic acid*.

Sodium metastannate, Na_2SnO_3 , is formed by adding an excess of sodium hydroxide to stannic hydroxide gel or by fusing stannic oxide with sodium carbonate:



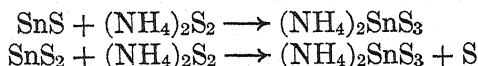
It is used in making cotton cloth fireproof, in weighting silk, and as a mordant. The soluble stannate enters into the fibers of the fabric and is there precipitated by ammonium hydroxide or by steam.

Plumbic hydroxide, $\text{Pb}(\text{OH})_4$, is not known, but plumbates derived from it can be obtained. Two of these are of interest. One is a red compound of the composition Pb_2O_3 , but is really a plumbous salt of metaplumbic acid, H_2PbO_3 , and its formula may be written PbPbO_3 or $\text{PbO} \cdot \text{PbO}_2$. The other is the pigment *red lead*, which is a plumbous salt of orthoplumbic acid (H_4PbO_4) and has the composition Pb_2PbO_4 or Pb_3O_4 . When treated with nitric acid, two thirds of the lead in red lead is converted into lead nitrate, while the other third forms the dioxide:

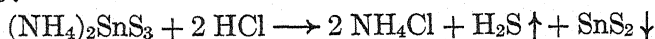


As a pigment red lead is especially effective in protecting structural steel from rust. Mixed with oil it forms a paste used in making joints in gas pipes gastight.

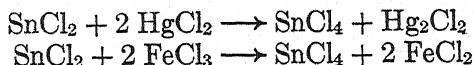
The sulfides of tin and lead. Apart from the native ore galenite, PbS , the sulfides of tin and lead are of interest chiefly in chemical analysis. From an acid solution of their salts, hydrogen sulfide precipitates *black* PbS from *all* simple lead salts; *brown* stannous sulfide, SnS , from stannous salts; and *yellow* stannic sulfide, SnS_2 , from stannic salts. All these sulfides are insoluble in dilute acids, but the sulfides of tin dissolve in yellow ammonium sulfide ($(\text{NH}_4)_2\text{S}_2$) to form *thiostannates*, while lead sulfide does not dissolve:



From these solutions stannic sulfide is precipitated by the addition of acids:



The halogen compounds of tin and lead. *Stannous chloride* is made by dissolving tin in hydrochloric acid, and crystallizes from solution as the hydrate $\text{SnCl}_2 \cdot 2 \text{H}_2\text{O}$, often called *tin salt*. It is used as a mordant in the dye industry and also as a reducing agent. The stannous ion of all simple stannous compounds tends to pass into the quadrivalent stannic ion, as illustrated in these equations:

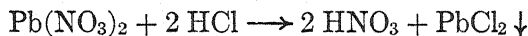


Anhydrous stannic chloride, SnCl_4 , is prepared industrially by treating tin scrap (or even used tin cans) with chlorine gas. It is a heavy colorless liquid which boils at 114° and freezes at -30° . In moist air it reacts vigorously with the water vapor and forms hydro-

gen chloride and dense clouds of stannic oxide. Stannic chloride dissolves in water, with strong heat evolution and with considerable contraction of volume. From such a solution a number of hydrates have been prepared, of which the pentahydrate, $\text{SnCl}_4 \cdot 5 \text{H}_2\text{O}$, is the usual one.

From solutions of this salt in hydrochloric acid a compound called *chlorostannic acid*, H_2SnCl_6 , can be isolated; the corresponding *fluorostannic acid*, H_2SnF_6 , is also well known. These yield long series of salts, of which ammonium chlorostannate, $(\text{NH}_4)_2\text{SnCl}_6$ (called *pink salt*), is the most important. This salt, as well as stannic chloride, is used in weighting silk and cotton cloth and as a mordant. The compounds of tin with bromine or iodine require no special mention.

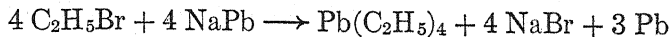
Lead chloride, PbCl_2 , is a well-crystallized colorless salt, moderately soluble in hot water and nearly insoluble in cold water. It is precipitated from acid solutions when hydrochloric acid is added to a solution of a lead salt:



Lead tetrachloride, PbCl_4 , is a very unstable heavy liquid that spontaneously loses chlorine, as does manganese tetrachloride (p. 286), and is reduced to ordinary lead chloride.

Other compounds of lead. Not many other compounds of tin have large uses in the arts and industries, but some lead compounds are of much importance and will be described briefly.

Lead tetraethyl ($\text{Pb}(\text{C}_2\text{H}_5)_4$). This is a covalent compound of quadrivalent lead that has come into wide use as an "antiknock" in motor gasoline. A very little of it greatly improves the quality of a motor fuel for high-compression gasoline engines; but since it is a poisonous compound, gasoline containing it (ethyl gas) should not be used for household purposes. It is made by first making an alloy of sodium in lead of about the composition NaPb , and treating this alloy with ethyl bromide, $\text{C}_2\text{H}_5\text{Br}$ (or ethyl chloride):



Lead carbonates. Normal lead carbonate, PbCO_3 , can be prepared as a white crystalline precipitate by treating a solution of a lead salt with sodium bicarbonate. A basic carbonate, $2 \text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$, is of much more industrial importance than the normal salt because of its wide use in the manufacture of paints. In commerce it is called *white lead*. A large percentage of all the lead produced goes into the manufacture of white lead and other lead pigments.

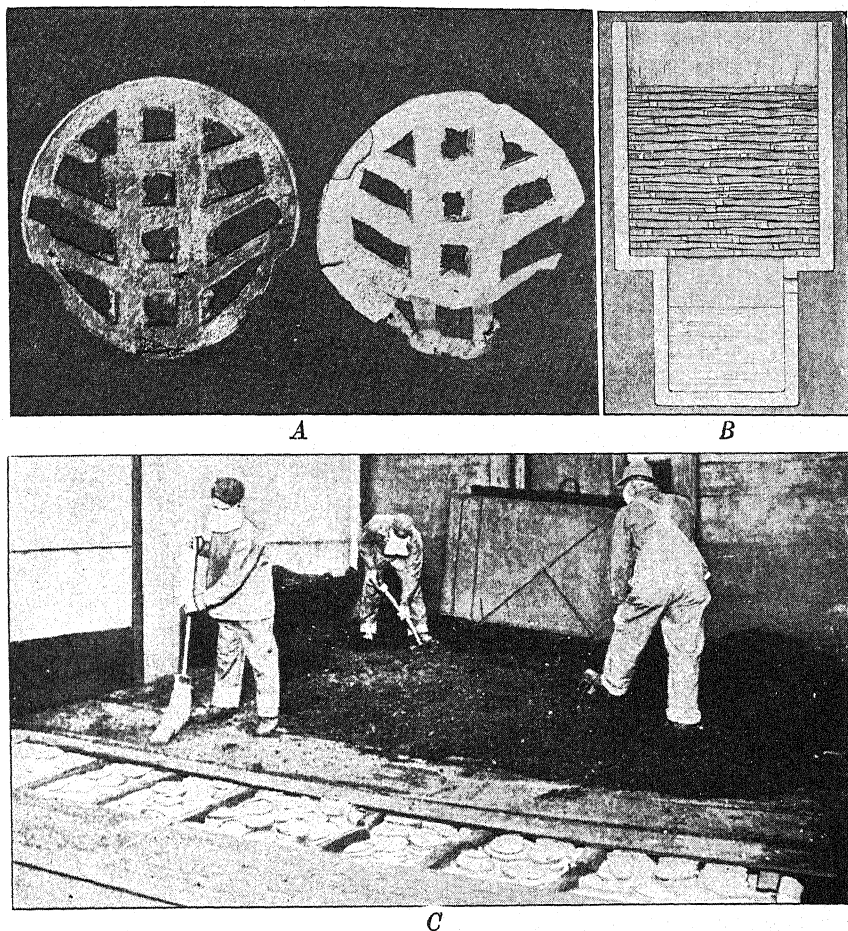


FIG. 365. *Steps in Making White Lead by the Dutch Process*

A, lead plates (buckles) before and after exposure to acetic acid and carbon dioxide. B, the lead plates placed in a crock, the lower part of which is filled with acetic acid. C, the crocks filled with the lead plates and acetic acid are placed in tiers and covered with spent tanbark (the bark of a tree rich in tannin, such as oak bark). The tanbark slowly ferments, setting free carbon dioxide. Enough heat is given off in this process to vaporize the acetic acid. The acetic acid and the carbon dioxide together convert the lead into white lead. The workmen remove the tanbark after the action is complete. The lead plates, now converted into white lead, are seen where the covering has been removed.

Manufacture of white lead. The old and still standard way of making white lead is called the *Dutch process* because it was devised and first used in Holland in the seventeenth century. In this process metallic lead is cast in the form of plates and is exposed to carbon dioxide and the vapors of acetic acid, as explained in Fig. 365.

The Dutch process is a very slow one, and more rapid ones have been devised that give very satisfactory products. One process depends upon electrolysis. The anode is a heavy lead plate dipping into a solution of sodium acetate and acetic acid; the cathode is an iron plate dipping into a solution of sodium carbonate; and the two solutions are prevented from mixing mechanically by a porous diaphragm. The lead ions on their way to the cathode meet the CO_3^{--} ions near the cathode and precipitate as the basic carbonate. The acetic acid set free attacks the lead anode.

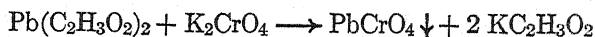
In a second process very finely divided lead, together with dilute acetic acid, is slowly rotated in barrel-shaped cylinders in which a regulated pressure of carbon dioxide is maintained.

Lead nitrate ($\text{Pb}(\text{NO}_3)_2$). This salt is readily obtained by dissolving metallic lead or litharge in nitric acid. It crystallizes in octahedra and is easily soluble in water.

Lead acetate ($\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$). The acetate is obtained by dissolving litharge in concentrated acetic acid, from which it crystallizes in snow-white monoclinic crystals of the composition $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3 \text{H}_2\text{O}$. The alchemists called it *sugar of lead* because of its sweetish taste. The nitrate and acetate are the important *soluble* salts of lead.

Lead sulfate (PbSO_4). Lead sulfate is a white crystalline solid, insoluble in water and dilute acids. It is therefore formed as a precipitate whenever the ions Pb^{++} and SO_4^{--} are brought together in solution. Sublimed White Lead is a trade name given a white pigment made by heating galena (PbS) in a current of air to a suitable temperature. Its composition may be represented as a mixture of lead sulfate, lead oxide, and a little zinc oxide.

Lead chromate (PbCrO_4). This bright-yellow salt, called *chrome yellow*, results as a precipitate when solutions of a lead salt and a chromate are brought together:



By boiling the normal chromate with a solution of an alkali a brick-red basic salt is obtained, called *chrome red*, which has the formula $\text{PbCrO}_4 \cdot \text{PbO}$. Both the *chrome yellow* and the *chrome red* are used as pigments.

Lead arsenate ($\text{Pb}_3(\text{AsO}_4)_2$). This compound is a white insoluble powder difficultly soluble in water, prepared by treating lead acetate with sodium arsenate. It is extensively employed as an insecticide.

GERMANIUM AND THORIUM

Germanium. Germanium was discovered in 1886 by Winkler, in connection with some analyses of the rare mineral *argyrodite*. His analyses failed to account for from 6 to 7 per cent of the mineral, and a long and

careful search resulted in the discovery of the new element. It was found to fulfill in a remarkable way the predictions of Mendeléeff for the properties of an undiscovered element which should follow silicon in Group IV, and which he provisionally named ekasilicon. It occurs in exceedingly small percentages in many American zinc ores (0.01 per cent) and the residue from zinc stills is the chief source of the element. Germanium is a brittle, crystalline, metallic substance which has a density of 5.36 and melts at 958.5° . It forms two oxides, of the formulas GeO and GeO_2 , each of which is amphoteric in character. Its compounds resemble those of tin very closely.

Thorium. Thorium was discovered by Berzelius in 1828 and named in honor of the Scandinavian god Thor. For the most part, it is found in very small percentages in various minerals, especially those that are rich in the "rare earths" (p. 612). Industrially its compounds are obtained from *monazite sand*. This is a heavy sand that consists of cerium phosphate associated with the phosphates of other rare earths and of thorium. The best quality of monazite sand comes from India and Brazil.

Compounds of thorium are obtained from monazite for the manufacture of gas mantles, which consist of 99 per cent of thorium oxide, ThO_2 , and 1 per cent of cerium oxide, Ce_2O_3 . The production of these mantles has declined greatly in recent years because of the widespread use of electric lights. The chief scientific interest in thorium lies in the fact that the element and all its compounds are radioactive, like uranium and its compounds. In its chemistry thorium is quadrivalent in all its compounds, and always plays the part of a base. The metal itself is very difficult to obtain in really pure form.

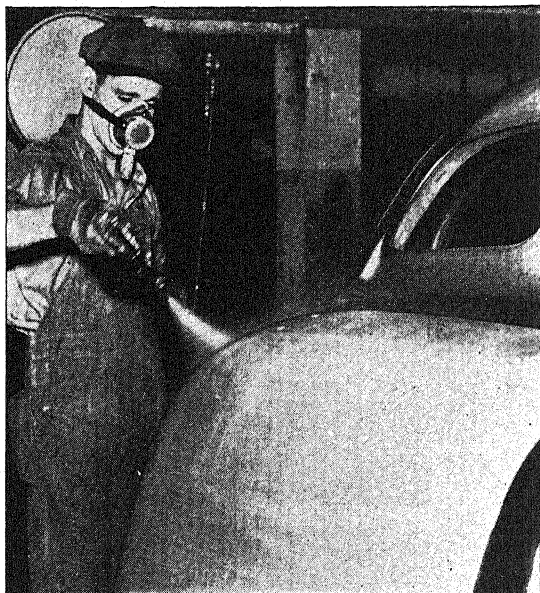
PAINTS, VARNISHES, LACQUERS

The nature of paints. A paint consists of two essential components: the vehicle and the pigment.

1. **The vehicle, or liquid medium.** The liquid portion of a paint consists of several components: (1) A *drying oil*, such as linseed oil, obtained from flaxseed, which will take up oxygen from the air and dry to a hornlike substance. (2) A *thinner*, consisting of turpentine or mineral spirits from petroleum, to reduce the viscosity to a suitable consistency for working. Such a thinner will evaporate after the paint has been applied. (3) A *drier*. This is a catalyst to promote the drying. The driers are often special soaps, made by boiling various inorganic compounds with the drying oil or sometimes with organic acids not found in the drying oil. The inorganic compounds commonly used are oxides of manganese, lead, cobalt, or various borates, hydroxides, acetates, sulfates, carbonates, and chlorides.

2. **The pigment.** The pigment, or solid part of the paint, consists of finely divided materials chosen so as to give the desired surface and color. The materials must also possess a good "hiding" power; that is, the surface

painted must not be visible through them. The pigment may be a white solid, such as white lead, zinc oxide, or lithopone.



General Motors Corporation

FIG. 366. *Spraying an Automobile Body with Lacquer*

Titanium dioxide, either alone or mixed with other compounds, such as barium sulfate, calcium sulfate, and magnesium silicate, has come into wide use. The pigment also may be a colored compound, such as iron oxide (red), chromium oxide (green), Prussian blue, carbon-black, as well as a wide variety of organic compounds. Color pigments are sometimes prepared by precipitating a colloidal compound in the presence of an organic dye of the desired color. The dye is adsorbed by the precipitate, which thus acquires the color of the dye. Such pigments can be pre-

pared in endless variety, and are called *lakes*. The use of these lakes as pigments, however, is diminishing.

The nature of varnishes. A varnish, like a paint, may be considered to be made up of a solid (nonvolatile) portion and a liquid medium.

1. **The solid portion.** Formerly the solid portion consisted exclusively of natural gums or resins obtained from certain trees, together with resin-like bodies, such as rosin obtained from pine trees. At present the nonvolatile solids used are largely synthetic gumlike substances. An important group of such substances is made by heating anhydrides like phthalic anhydride with glycerin (or other polyhydric alcohols) and fatty acids.

2. **The liquid portion.** In the usual type of varnish the nonvolatile solids, together with a drier, are dissolved in some appropriate oil, of which a score or more are now used. Prominent among these are dehydrated castor oil, soybean oil, fish oil, and tung oil. The tung oil is obtained from the nuts of the tung tree, a native of China, but now grown in some of the Southern states. It was formerly very largely used, but at present, because of the cost, it is being replaced by the cheaper oils mentioned above.

The nonvolatile solids are dissolved by heating the mixture; and after boiling, the product is thinned with turpentine or some similar volatile solvent, such as benzine. On exposure to the air, the thinner evaporates,

and the oil oxidizes and dries along with the nonvolatile solids. It was the introduction of synthetic resins that made possible the manufacture of the popular four-hour varnishes.

In another type of varnish, called *spirit* varnish, the nonvolatile solid is dissolved in a volatile liquid, such as turpentine or alcohol. On exposure to air, the solvent evaporates, leaving a film of the solids.

The nature of lacquers. A lacquer is a special kind of varnish. As made at the present time, lacquers are composed of (1) cellulose derivatives (known in the trade as "nitrocottons"); (2) a resin, including any of the synthetic varnish resins; (3) a *plasticizer*, such as castor oil and certain organic phosphates, to prevent cracking or breaking on drying; (4) a solvent, such as ethyl acetate or similar esters; (5) a diluent, usually a coal-tar hydrocarbon or a similar petroleum distillate; (6) a pigment color, either organic or mineral. The plasticizers, solvents, and diluents named above are simply examples. New ones are constantly coming into use.

Lacquers dry so rapidly that they are best applied by a spray gun (Fig. 366). By their use an automobile can be sent from the paint shop in two days instead of the two weeks formerly required. Indeed, most surfaces are dry enough to be used a few hours after they have been lacquered. It is not too much to expect that future developments may make it possible for a man to have his automobile painted while he eats his lunch.

Questions

1. Tin and lead were confused by the ancients. How could you tell samples of the two metals apart most easily?
2. Aside from that of tin, what other examples can you name of transformation of an element or compound from one form into another at a definite transition temperature?
3. If sheets of aluminum were to be galvanized with zinc, what factors would determine which metal would corrode?
4. Suggest two methods for recovering tin from old tin cans.
5. Why is tin pipe rather than lead pipe used for carrying distilled water from one part of a laboratory to another?
6. (a) What compounds analogous to fluostannic acid have we studied? (b) What is the valence of the central element in each case? (c) What other elements might be expected to form similar compounds?
7. What hydroxides of metals besides those of tin and lead are soluble in alkalis?
8. Why are white paint pigments other than white lead now so extensively used, particularly in manufacturing cities?
9. What are the differences in the reaction of nitric acid on tin and on lead?

10. What other elements give acids of formula similar to that of stannic acid?
11. What should you expect to be the reaction between Pb_2O_3 and nitric acid?

Problems

1. How much lead peroxide can be obtained from 100 g of minium by the action of nitric acid?
2. If we assume that metallic lead costs 3 cents a pound and white arsenic 4 cents, which of the two would be the more expensive material in the manufacture of lead arsenate?
3. One hundred grams of potassium fluostannate was transformed into the corresponding salt of fluozirconic acid. What did the product weigh?
4. A sample of cast iron weighing 1 g was dissolved in hydrochloric acid and oxidized to ferric chloride. This was reduced to ferrous chloride with a solution of stannous chloride, 1.6 g being required. What was the percentage of iron in the sample?
5. A sample of 1 g of white lead was dissolved in acetic acid, and 52 cc of carbon dioxide (standard conditions) was obtained. What was the percentage purity of the sample?

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Chemistry in Agriculture; Purification of Water Supplies

SOILS

Uses of the soil. Ordinarily we think of the soil as useful because it makes possible the growth of all the plants and trees that directly or indirectly provide our food. With more careful thinking we realize at once that plants and trees are the source of many valuable products other than foods. We obtain rubber from rubber trees; drugs, such as quinine, from cinchona bark; and morphine from poppy pods. We also obtain from plants and trees fibers such as cotton and linen for clothing; wood for our homes; oils and resins for paints. Various substances from plants and trees are often the source materials for making hundreds of useful articles; for example, many resins and plastics (p. 531) are made from sap or seeds, and so many automobile parts are made from these plastics that one enthusiastic engineer has said (speaking figuratively, of course) that the time may come when we shall "grow" automobiles.

The percentage of farm products used for purposes other than for food is steadily increasing. Realizing that we have merely made a beginning in this direction the Federal government has established a number of research laboratories in which trained scientists are seeking new uses for farm products. "Chemurgic products" is a name coined to designate the industrial uses for farm crops; and it may be that the serious problems confronting the farmer may be solved by finding new uses for the things he can grow. The government may then be urging increased rather than diminished production.

Origin and composition of soils. The soil has been formed by the agelong action of rain, ice, wind, atmospheric gases, and the growth of vegetation on the surface rocks of the earth. These agencies have produced an exceedingly complex and variable mixture of minerals, consisting principally of silicon dioxide, feldspars, kaolin (the chief constituent of clays), carbonates, and phosphates. The most abundant metallic bases of these minerals are aluminum, calcium, magnesium, and iron. Some compounds of potassium, nitrogen, and sulfur are always present, often in very small percentages; and all fertile

soils contain organic materials (*humus*) derived from animal and vegetable remains, together with bacteria of various kinds. It is probable that bacteria were among the first living organisms to appear on earth.

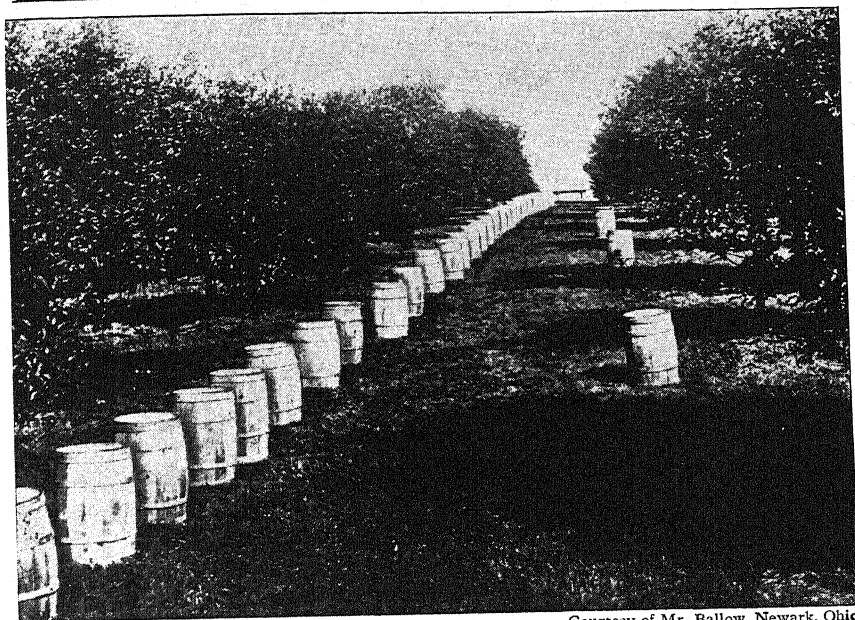
FERTILIZERS

The necessity for fertilizers. With the exception of carbon dioxide (and possibly a little oxygen) absorbed from the air, the growing plant gets its nutriment from the soil. In order that vegetation may thrive it is essential, therefore, for the soil to contain an adequate supply of suitable plant food. The natural supply is continually being drawn upon by growing plants; and for the soil to retain its fertility the ingredients so withdrawn must be returned to it and in a form that can be assimilated by the plants. It is to supply this need that fertilizers are used (Fig. 367).

Constituents of fertilizers. While a number of elements are essential to the growth of plants, experience has shown that in general the fertility of the soil may be maintained by the addition of four substances: (1) nitrogenous matter, (2) phosphates, (3) compounds of potassium, and (4) compounds of sulfur. It should be added, however, that our knowledge as to what substances are essential to plant growth is far from complete. Recent experiments indicate that in addition to the elements long regarded as the only essential ones (carbon, oxygen, hydrogen, nitrogen, phosphorus, potassium, calcium, magnesium, sulfur, and iron), small percentages of the following are also necessary for the growth of at least certain plants: manganese, zinc, copper, silicon, chlorine, aluminum, and boron. The required amounts of these are very small, and it is probable that most soils have the necessary supply; if not, they must be provided and in a form that the plant can use. This subject is an interesting and important one for investigation, and the experiment stations of the national government and of the various states spend large sums of money annually in experimenting on the effects of fertilizers. At present extensive experiments on fertilizers are being carried on by the national government at Muscle Shoals, Alabama.

Sources of fertilizers. The industrial sources of each of the constituents of fertilizers are as follows:

1. **Nitrogenous matter.** This is obtained from a number of sources: sodium nitrate, ammonium sulfate, ammonium phosphate, cyanamide (p. 582), and urea (p. 462); also from nitrogenous organic matter, such as dried blood, the waste from slaughterhouses, and animal manures. Formerly we secured all our sodium nitrate



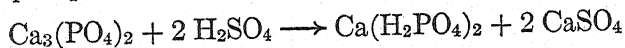
Courtesy of Mr. Ballow, Newark, Ohio

FIG. 367. View of an Ohio Apple Orchard, Showing the Effect of Fertilizers

The row of twelve trees on the left, fertilized with sodium nitrate and calcium acid phosphate, produced thirty barrels of apples. The unfertilized row of twelve trees on the right produced only three barrels

from Chile (p. 586) and ammonium sulfate from by-product ammonia in coal distillation (p. 482). At present a large percentage of these compounds is made from synthetic ammonia prepared by the Haber process.

2. Phosphates. Ground bones are especially valuable, since they contain some nitrogen in addition to calcium phosphate. This source is entirely inadequate, and the great supply comes from rock phosphates, which contain about 70 per cent of calcium phosphate. These rock phosphates are quarried in large tonnages, especially in Florida and Tennessee, and low-quality material can be concentrated by flotation. Since calcium phosphate is practically insoluble, it must undergo chemical treatment to make it available as a plant food. It is ground and treated with sulfuric acid, which converts the insoluble phosphate into a soluble calcium hydrogen phosphate:



The resulting mixture of calcium hydrogen phosphate and calcium sulfate is a powder known commercially as *superphosphate of lime*.

Since phosphoric acid is now produced cheaply by the oxidation of phosphorus, phosphate rock is sometimes treated with this acid rather than with sulfuric acid :



A very concentrated fertilizer is thus produced, which saves transportation costs. Slags from the production of steel from ores containing phosphorus are sometimes used in making fertilizers.

3. Potassium compounds. The potassium for all industrial uses comes from salt deposits of potassium compounds, chiefly KCl (sylvite), $\text{KCl} \cdot \text{MgCl}_2 \cdot 6 \text{H}_2\text{O}$ (carnallite), and $\text{MgSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 2 \text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$ (polyhalite). For many years the agricultural world was dependent on the salt beds of Stassfurt (Germany) and of Alsace (France) for its fertilizer potassium. Similar but less extensive beds have been discovered more recently in a number of countries — for example, in the United States, in New Mexico (Carlsbad) and Texas. Potassium chloride is also extracted from Searles Lake, California, and to a lesser extent from brines, sea water, and from certain mineral rocks. We still import many thousands of tons of potassium salts from Europe, partly because our deposits have not been fully developed and partly because the Eastern states find transportation cheaper from Europe than from the Far Western states.

4. Sulfur compounds. Reference to paragraph 2 will show that the ordinary superphosphate of lime contains calcium sulfate, and this sulfur compound is beneficial to most soils. For growing certain crops ground gypsum is sometimes added as a fertilizer.

5. Plant-growth substances. In addition to the fertilizing agents already described it has been found that minute quantities of certain complex organic chemicals enormously stimulate plant growth (especially root growth). These seem to act much as the vitamins of food or the hormones of the glands of the animal body. These plant-growth substances are now available in fertilizers specially prepared for use in flower beds and greenhouses.

Soilless growth of plants (hydroponics, or chemiculture). In the growth of plants the soil has a double function: it holds the plant foods, and it provides anchorage for the roots that support the plant. Both functions may be provided for successfully without any soil. The plant may be artificially supported, and the roots may find nourishment in water to which has been added the foods essential to plant growth in suitable form and concentration. Garden vegetables and flowers may be grown in this way as window gardens or

in greenhouses and with surprising results, but this mode of cultivation is not likely to be extended to field crops.

Commercial fertilizers. As a rule, commercial fertilizers are mixtures of two or more of the essential plant foods. The composition of the fertilizer is adjusted to the crop to be grown and to the character of the soil under cultivation. For example, potatoes thrive best in a soil rich in potassium compounds, while wheat is benefited more by phosphates. These fertilizers are usually sold in bags on which are stamped three figures, such as 2-12-6. The first figure gives the percentage of nitrogen in the fertilizer, the second the percentage of phosphorus (calculated as P_2O_5), and the third the percentage of potassium (calculated as K_2O).

Liming soils. Sometimes a soil becomes sour, or acid, owing to the formation of acids from decomposing vegetable matter or from the oxidation of minerals such as pyrite. Certain plants, such as mosses, sorrel, and huckleberries, will thrive in acid soil, but grass, clover, and grain crops will not. Such soil must be *sweetened* by spreading calcium hydroxide (slaked, or hydrated, lime) or ground limestone upon it to neutralize the acids. The process is called *liming* the soil. An acid soil may be detected by moistening strips of blue litmus and covering them for a few minutes with the moist soil.

INSECTICIDES AND FUNGICIDES

The problem. Anyone who has had even a little experience in growing plants or animals knows how hard it is to keep them free from organisms that either kill them or impair their growth. So serious are the problems suggested by this experience that our entire food supply is threatened unless they can be solved. The national government and the state experiment stations are constantly carrying on experiments to find effective ways and means of fighting the pests that are a threat. Some of these pests have been brought under control, but others have not. For example, a blight has killed practically all our chestnut trees, and the elms seem doomed to follow unless some way is found to control the disease that is now exacting a heavy toll. Many of these pests are visible insects, such as cattle ticks and aphids, while others, more difficult to combat, are fungi (molds) and bacteria.

The attack. The general method of attack is to treat the plants or animals with a spray or dip containing chemicals that kill the destructive organisms. These chemicals vary according to the pest to be conquered. Those used for insects are called *insecticides*; those for fungi, *fungicides*. A few of the most important of these two



FIG. 368. *Airplanes Are Sometimes Used in Dusting Insecticides on Plants*

classes are the following: (1) *Arsenic compounds*, largely used as insecticides (Fig. 368), include lead arsenate, $\text{Pb}_3(\text{AsO}_4)_2$, calcium arsenate, $\text{Ca}_3(\text{AsO}_4)_2$, and Paris green, a complex double salt of copper acetate and copper arsenite. (2) *Lime-sulfur spray* is an aqueous solution of sulfur compounds, chiefly the sulfides CaS_4 and CaS_5 . It is made by heating a mixture of calcium hydroxide, sulfur, and water and acts both as an insecticide and as a fungicide. It is widely used, especially in spraying fruit trees (Fig. 369). (3) *Bordeaux mixture* is a complex fungicide made by adding calcium hydroxide to a cold solution of copper sulfate. (4) *Nicotine sulfate* is very poisonous to certain insects, such as aphids and leaf hoppers. (5) A mixture of *cresols* obtained from coal tar (p. 514) acts as an insecticide and is the basis of many common disinfectants. (6) *Hydrocyanic acid* is very effective in keeping citrus fruit trees free from injurious pests.

As all six of these agents are toxic to human beings, and two of them (nicotine sulfate and hydrocyanic acid) very toxic, great care must be taken in the use of them. Two other products have come into use because they are not poisonous to man or to any warm-blooded animal. These are *pyrethrum* and *rotenone*. Pyrethrum is a

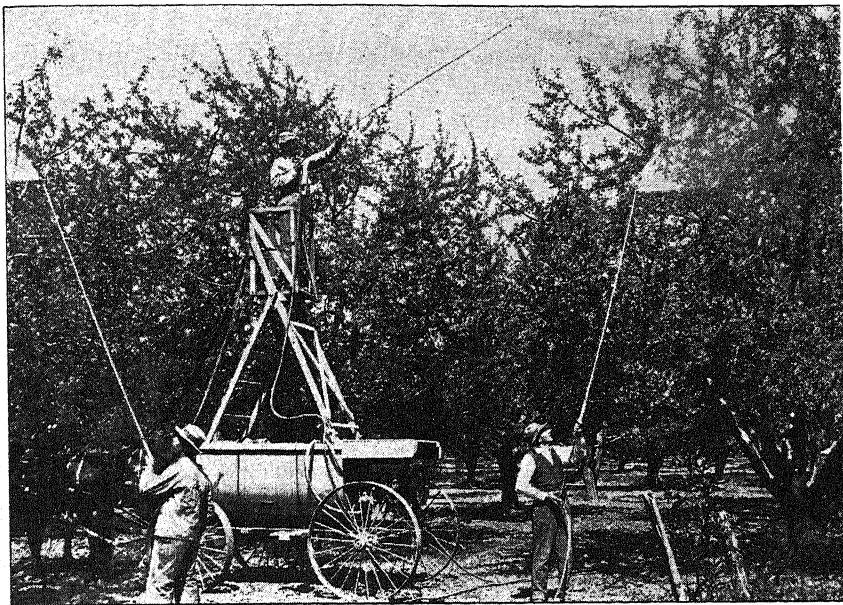


FIG. 369. *Spraying Apple Trees with Lime-Sulfur Spray*

powder obtained from certain plants belonging to the chrysanthemum family, while rotenone comes from the roots of plants of the derris family. They are insecticides and seem to act by paralyzing the nervous system. The common fly repellents usually consist of a solution of the active principles of pyrethrum dissolved in a paraffin oil.

THE HEALTH-PURIFICATION OF WATER

Pure water. We have seen that natural waters are never chemically pure, but always contain more or less mineral and organic matter (p. 163). To obtain chemically pure water from natural waters all foreign matter must be removed, and this is done by distillation. Distilled water has important uses in scientific investigations, for filling storage batteries, and as a solvent for medicines.

Requirements for a public water supply. When we say that water for drinking purposes is *pure*, we mean that there is nothing in it to endanger health. The menace to health of an impure water is not due to the mineral matter that it may contain, nor to the lifeless organic matter, but to definite kinds of bacteria and other micro-

organisms that are likely to accompany the organic matter. A safe drinking water must be free from these microorganisms, and should have other qualities as well. In his treatise entitled *Water Supply and Treatment*, C. P. Hoover states that the requirements for a public water supply are as follows:

1. That it shall contain no organisms which cause disease.
2. That it be sparkling, clear, and colorless.
3. That it be good-tasting, free from odors, and preferably cool.
4. That it be reasonably soft.
5. That it be neither scale-forming nor corrosive.
6. That it be free from objectionable gas, such as hydrogen sulfide, and objectionable minerals, such as iron and manganese.
7. That it be plentiful and low in cost.

Bacteria. These are low forms of microscopic life. They exist in countless numbers in the soil, in dust and dirt, in the atmosphere, and especially in refuse matter. They are literally everywhere. There are many different kinds of bacteria. Some of them are of great service; and we grow certain species for definite uses, just as we grow other organisms. Other species are the direct cause of certain diseases. It is known that many transmissible diseases, such as typhoid fever, are due to bacteria, each disease being the result of the growth of a definite kind of organism in the body. It is easily possible for these bacteria to find their way, through sewage from persons afflicted with a disease, into a poorly protected water supply; and it is in this way that typhoid fever is spread. Bacteria are killed by heat, which leads to the common practice of boiling a sample of water to render it safe for drinking. As they are more resistant to cold, however, ice frozen from impure water is not safe for human consumption.

Importance of purifying water. An adequate supply of wholesome drinking water is of the utmost importance to a community, and the problem of securing it becomes increasingly difficult as the population increases. Our cities and many of our towns find it necessary to take their water supply from rivers and lakes. With increasing population it is impossible to keep such waters from contamination with sewage and other organic matter, which are natural carriers of disease-producing microscopic organisms.

Effect of water purification on disease. Fig. 370 shows the effect of water purification in diminishing the deaths due to typhoid fever in a typical city (Columbus, Ohio). Before the water was purified, typhoid fever was always prevalent; for example, in 1904 there were over 120 deaths from this disease for each 100,000 inhabitants. After the construction of a water-purification plant, in 1909, the deaths due to this disease fell off greatly, amounting in 1920 to only 3 for each 100,000 of population; and at present the disease

is almost unknown in this city. (In 1938 there was only one case of typhoid fever in the city, and this was due to the use of impure water in an adjoining village.) The purification of the water supply is therefore an important problem.

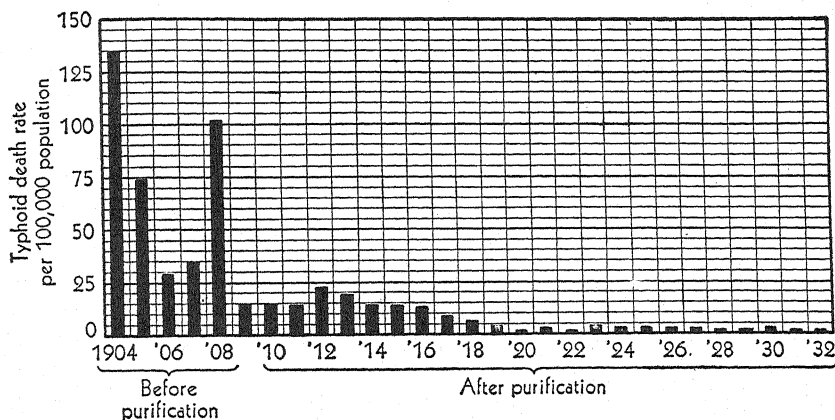


FIG. 370. *Effect of Water Purification on Death Rate Due to Typhoid Fever*

Purification of water on a large scale. Such processes as boiling and distillation are not practicable in dealing with the large quantities of water required to meet the demands of cities and towns. In Columbus, Ohio, for example, the city water system is drawn upon for an average of 33,000,000 gal daily, while in Chicago the amount is 920,000,000 gal (247 gal per inhabitant). A number of different methods of purifying water on a large scale are now in use. These methods differ in detail, but all are alike in that the water is treated with chlorine, to destroy any microorganisms present. The amount of chlorine ordinarily added varies from 2 to 5 lb per 1,000,000 gal of water. The different methods are as follows:

1. **Treatment with chlorine alone.** This is the simplest method, but it can be effectively employed only when the natural water used is clear, as is the case in New York.

2. **Filtration through slow sand filters and subsequent treatment with chlorine.** These filters are constructed of sand and gravel, as shown in Fig. 371. The water filters through the sand and gravel and passes into the porous pipe A, from which it is pumped into the city mains. Some of the impurities are strained out by the filter, while others are decomposed by the action of certain kinds of bacteria which collect in a jellylike layer on the surface of the filter. Chlorine is added to the filtered water as an extra precaution.

3. *Treatment with aluminum sulfate (or some related compound, such as ferrous sulfate), filtration, and subsequent treatment with chlorine.* Most natural waters are basic in character. When aluminum sulfate is mixed with such waters, hydrated aluminum oxide

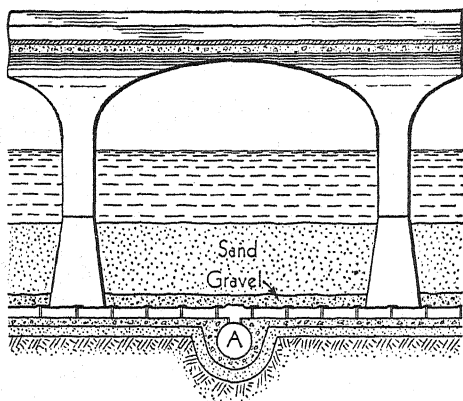


FIG. 371. Diagram of a Slow Sand Filter

(aluminum hydroxide) is formed (p. 603) as a colloidal dispersion throughout the water. This slowly coagulates and, as it settles, carries down with it any suspended matter present, including bacteria and coloring materials. After the precipitate has settled, the supernatant water is drawn off and run through rapid sand filters. It is then treated with a small amount of chlorine as a final precaution.

Removal of objectionable tastes and odors in city water supplies. Not infrequently city water supplies acquire a disagreeable taste or odor. These may be due to a number of causes, such as the presence of certain microscopic organisms or algae, dissolved gases, or materials which find their way into the water from industrial plants. Overchlorination may also produce an unpleasant odor and taste. These objectionable qualities may be removed by different methods. The gases present may be removed by aeration. Activated carbon is a very efficient agent for the purpose; the water may be filtered through a bed of granular carbon, or a small percentage of activated carbon may be added directly to the water and, after allowing a short reaction period, be removed by filtration. Objectionable qualities resulting from overchlorination may be remedied by the addition of a small percentage of sulfur dioxide or sodium sulfite.

THE INDUSTRIAL PURIFICATION OF WATER

Softening of hard waters. Most of the natural waters have varying percentages of compounds of calcium and of magnesium, derived from contact with various rocks. All such waters are called *hard*.

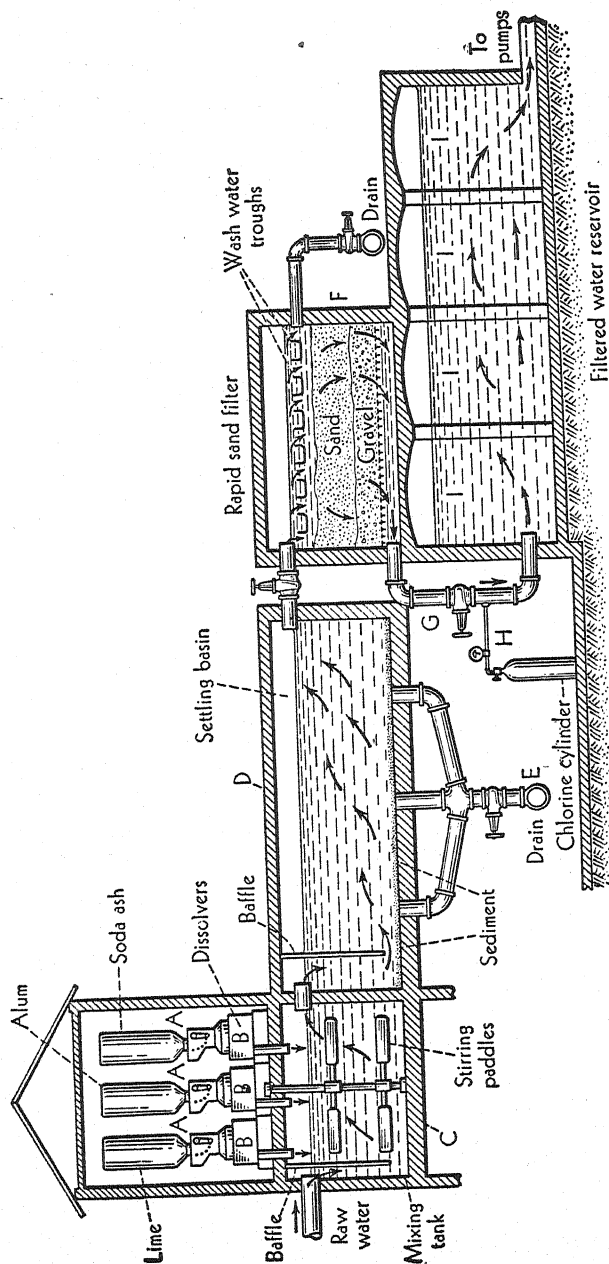


Fig. 372. *Diagram Showing the Essential Parts of a Plant for Softening and Purifying the Water Supply of a City*

The impure raw water enters the mixing tank *C*, where it is thoroughly mixed with the purifying and softening reagents entering at the top of the tank, as shown in the diagram. The mixture then flows into the settling basin *D* (see also Fig. 373), where the solids formed by the action of the purifying reagents upon the water settle to the bottom and are drawn off through *E* from time to time. The water next flows through the rapid sand filter *F*, then through the pipe *G* (where the necessary chlorine is added at *H*) into the filtered water reservoir, and from this into the city mains. The rapid sand filters are cleaned by occasionally forcing a stream of water through them in the reverse direction. The water carrying the impurities flows out through the "wash water troughs" into the drain, as shown in the diagram

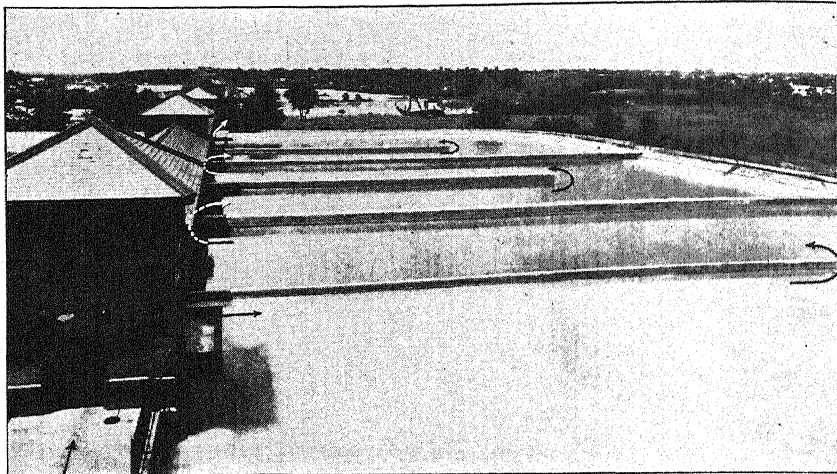
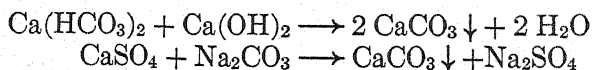


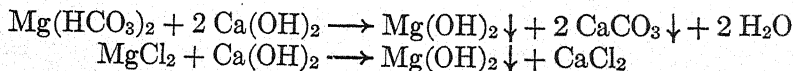
FIG. 373. *Picture of Settling Basins of the Water Works of Columbus, Ohio (Arrows Show Direction of Flow of Water). (See Fig. 372)*

These hard waters are objectionable in many ways. When used for cleansing purposes, much larger quantities of soap are required than with soft waters; and if they are used in steam boilers, deposits are formed, called boiler scale (p. 706). Hence many cities not only purify their water but soften it as well.

The method used to accomplish these two ends jointly is the same as the third method given above for purifying water, except that along with the aluminum sulfate there are added sufficient quantities of calcium hydroxide and sodium carbonate to precipitate the calcium and magnesium salts present (Fig. 372). The calcium and magnesium in hard waters are present as the acid carbonate, the sulfate, the chloride, or the nitrate. That portion of the calcium present as acid carbonate is precipitated by the calcium hydroxide added, while that present as sulfate, chloride, and nitrate is precipitated by the sodium carbonate. The reactions are expressed by the following typical equations:



The magnesium salts are precipitated by the calcium hydroxide in accordance with the following typical equations:



The calcium chloride formed according to the last equation reacts with the sodium carbonate as follows :



It will be seen from these equations that the calcium is precipitated as the carbonate, and the magnesium as the hydroxide. These two compounds are practically insoluble in water and settle out as the water slowly flows through reservoirs called *settling basins*. It is also evident from the equations that waters softened by this process contain sodium salts, but the presence of these is not objectionable unless the water is used for special purposes ; they have no effect on soap.

Some idea of the economy resulting from the softening of city water supplies may be inferred from the fact that the softening of the city water in Columbus, Ohio (population 300,000), has effected an estimated saving in soap alone amounting annually to more than \$500,000. An extensive investigation proved that in Illinois the average city of 40,000 inhabitants wastes about 1 ton of soap daily because of the hardness of the water, to say nothing of the loss of heat due to the formation of boiler scale.

The use of sodium hexametaphosphate in the treatment of water. When water is softened by the addition of calcium hydroxide and sodium carbonate, the reaction gradually slows down, so that several days may be required for completion. As a result, the water, after it enters the city mains, still contains a small percentage of calcium and magnesium salts which are slowly deposited in the pipes through which the water flows. In time this causes trouble by clogging the pipes ; and this is especially true when the water is used in steam boilers, since heat hastens the final reactions. Hall, a water chemist of Pittsburgh, has found that the addition to the water, either before or after it passes through the filter *F* (Fig. 372), of a small percentage of sodium hexametaphosphate, $(\text{NaPO}_3)_6$ (known by the trade name of Calgon), prevents further precipitation, and so the pipes are kept free from deposits. Just how the metaphosphate acts to prevent precipitation is not known. Only a very small percentage of it is required. For example, in Columbus, Ohio, only 2 lb of the metaphosphate per million gallons of water is required to prevent

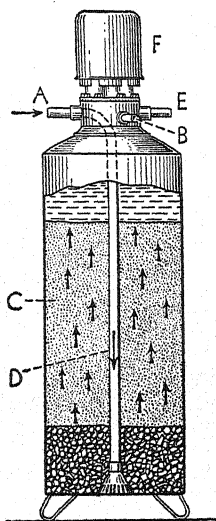
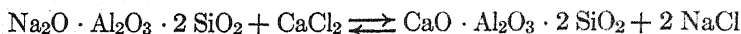


FIG. 374. A Diagram of the Zeolite Process for Softening Water

The hard water enters at *A* and flows to the bottom of the container through the pipe *D*. It is then forced upward through the zeolite *C*, which removes the calcium and magnesium ions. The resulting soft water flows out through the pipe *B*. From time to time a solution of sodium chloride, forced in at *E*, regenerates the zeolite

further precipitation. Solutions of the hexametaphosphate, as well as of sodium pyrophosphate, $\text{Na}_4\text{P}_2\text{O}_7$, are effective in dissolving scale after it has formed — for example, in cleaning the radiator of an automobile.

The zeolite process for softening water. The name *zeolite* is given to a mixture of complex sodium-aluminum silicates found in nature and also prepared synthetically for use in softening water. The sodium of the zeolite is replaced by the calcium and magnesium ions in hard waters when such waters are brought into contact with the zeolite, thus:



If now a saturated solution of sodium chloride is allowed to flow over the resulting calcium compound, the reaction goes in the opposite direction and

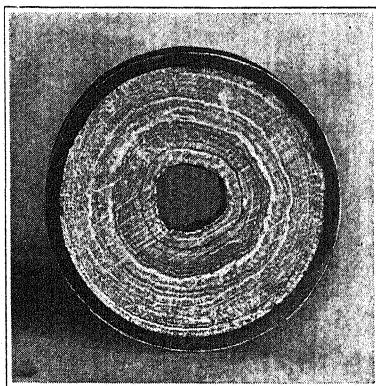


FIG. 375. Cross Section of a Boiler Tube, Showing the Deposit of Scale

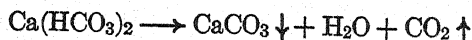
the zeolite is regenerated. In other words, the reaction is reversible and may be made to go in either direction by increasing the mass of the appropriate compound. In softening water by this process the zeolite is placed in a long drum and the hard water passed through the drum (Fig. 374). The apparatus is built in duplicate, so that the material in the one drum may be regenerated while that in the other drum is being used for softening the water. It is evident that water softened in this way will contain sodium salts, but these have no effect on soap.

While this method has been used largely for softening water on a small scale, especially in individual homes, it is now coming into use for softening city water supplies. It is not so efficient for removing calcium and magnesium when present as the acid carbonates as is the lime-soda process.

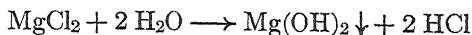
Boiler scale. When water which contains certain salts in solution is evaporated in steam boilers, a hard, insoluble material called *scale* deposits in the boiler. The formation of this scale may be due to several distinct causes:

1. **To the deposit of calcium sulfate.** This salt, while sparingly soluble in cold water, is almost completely insoluble in superheated water. Consequently it is precipitated when water containing it is heated in a boiler.

2. **To decomposition of acid carbonates.** As we have seen, calcium acid carbonate and magnesium acid carbonate are decomposed on heating, forming insoluble normal carbonates:



3. *To hydrolysis of magnesium salts.* Magnesium chloride and, to some extent, magnesium sulfate undergo hydrolysis when superheated in solution, and the sparingly soluble magnesium hydroxide is precipitated:



The scale adheres tightly to the boiler tubes in compact layers (Fig. 375) and, being a nonconductor of heat, causes much waste of fuel. It is very difficult to remove, owing to its hardness and resistance to reagents. Thick scale sometimes cracks, and the water, coming in contact with the over-heated iron, may cause an explosion. Moreover, the acids set free in the hydrolysis of the magnesium salts attack the iron tubes and rapidly corrode them. For these reasons water containing such salts should be softened before being used in boilers.

Questions

1. Upon what does the fertility of a soil depend?
2. Name the different ways of increasing the fertility of a soil.
3. Would the chemical analysis of soil tell the whole story as to its fertility?
4. We have to use at least three different insecticides in spraying different trees and plants. Why are so many necessary?
5. What properties would constitute the ideal insecticide?
6. Are any insecticides known that are poisonous to insects but not to human beings?
7. Give different meanings applied to the term *pure water*.
8. (a) What are the common impurities present in ordinary waters?
(b) To which of these is hardness due?
9. (a) What mineral constituents are commonly present in natural waters? Suppose you wished to soften such waters: (b) What chemicals would be required? (c) Write the equations for the reactions that would take place in the process.
10. States the advantages to be gained by a city in using pure, soft water.
11. How do you account for the fact that the sodium compounds formed in the softening of water have no action on soap?
12. (a) Why are chemists necessary in all water-purification plants?
(b) What are their particular duties?
13. Point out how it is possible to remove calcium compounds from water by adding another calcium compound.

Problems

1. Ordinary rock phosphate, used in making fertilizers, contains about 70 per cent of calcium phosphate. (a) What weight of sulfuric acid containing 45 per cent of H_2SO_4 is necessary to convert 1 ton of the rock phosphate into superphosphate of lime? (b) Why is such treatment necessary?

2. Lead arsenate, a common insecticide, is made by treating lead acetate with sodium arsenate. What weight of each of these compounds is necessary for the preparation of 100 lb of lead arsenate?

3. A certain city uses 30,000,000 gal of water daily. Suppose that this water contains 50 g of calcium acid carbonate and 20 g of calcium sulfate in 100 gal of water. What compounds and what weight of each would be required to soften the daily water supply?

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MORRISON. *Man in a Chemical World*. Chapter IV, entitled "Feeding Millions," tells of fertilizers.

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RIEGEL. *Industrial Chemistry*. Chapter VIII tells of fertilizers, and Chapter XIII of the purification of water.

SLOSSON and HOWE. *Creative Chemistry*. Chapter III, entitled "Feeding the Soil," tells an interesting story of fertilizers.

THOM. "Life in the Soil," *Scientific Monthly*, Vol. XLI, pp. 57-60. Tells of the many microorganisms present in the soil.

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Symposium on insecticides, *Industrial and Engineering Chemistry*, Vol. XXV, pp. 616-644. Contains a number of papers on the general subject of insecticides.

Some Metallo-Acid Elements

ELEMENT AND SYMBOL	ATOMIC WEIGHT	ATOMIC NUMBER	DENSITY	MELTING POINT	ELECTRONS IN SHELLS
Chromium (Cr) . . .	52.01	24	7.1	1615°	2:8:12:2
Manganese (Mn) . .	54.93	25	7.2	1260°	2:8:13:2
Vanadium (V) . . .	50.95	23	5.96	1710°	2:8:11:2
Columbium (Cb) . .	92.91	41	8.4	1950°	2:8:18:11:2
Tantalum (Ta) . . .	180.88	73	16.6	2996°	2:8:18:32:11:2
Molybdenum (Mo) .	95.95	42	10.2	2625°	2:8:18:12:2
Tungsten (W) . . .	183.92	74	19.3	3370°	2:8:18:32:12:2
Uranium (U)	238.07	92	18.7	1850°	2:8:18:32:18:12:2

The elements. With the exception of manganese, the elements in the table constitute the A families in Groups V and VI of the periodic table. These elements are brought together in one chapter because they are typical metals in all their physical properties, *while in their chemical characteristics they can all act as acid-forming elements.* For this reason *they are called metallo-acid elements.* It is chiefly either as free metals or as acids (and their salts) that these elements come into industrial uses.

Two of these elements, chromium and manganese, form many salts in which the metal atoms are simple cations, as well as acids in which the metal atoms are a part of covalent anion radicals. With the other six metals in the table the tendency to form simple cations of salts is either absent altogether or rather feebly developed. All the elements in the table have two or more stages in valence, and so each one forms a great many compounds.

It is convenient to study chromium and manganese together as one group and the other six elements as a second group.

CHROMIUM AND MANGANESE

General. Chromium and manganese have many characteristics in common. Both have more than two valences — chromium, 2, 3, and 6; manganese, 2, 3, 4, 6, and 7. In valences of 2 and 3 both metals form bases and corresponding salts like those of iron. In valences of 6 or 7 they form oxygen acids, such as H_2CrO_4 and

HMnO_4 . In its valence of 4 (MnO_2) manganese is amphoteric. Under reducing conditions all compounds of these elements pass into compounds of lower valences and form salts, while under oxidizing conditions compounds of lower valence are oxidized to ones of higher valence and form acids. Because of the ease with which these changes take place, compounds of these metals take part in many reactions of oxidation-reduction. The oxygen acids of both metals (and their salts) are powerful oxidizing agents and are used for oxidizing purposes.

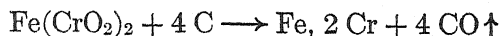
Ores of chromium and manganese. While both chromium and manganese are constituents of many minerals, and manganese, especially, is widely distributed in nature, the chief ore of chromium is chrome iron ore (chromite), $\text{Fe}(\text{CrO}_2)_2$ or $\text{FeO} \cdot \text{Cr}_2\text{O}_3$, and that of manganese is the dioxide, MnO_2 (pyrolusite). Both these minerals, as well as others of these metals, are found in various places in the United States, chiefly in Montana, Tennessee, Georgia, and Arkansas, but nearly always in low-grade ores unprofitable to work. We import annually about 250,000 tons of chromite and approximately three times as much pyrolusite. Soviet Russia and regions in Africa, Cuba, and India produce ores of both metals; and in addition Turkey and Greece produce chromite and Egypt and Brazil pyrolusite.

In recent years, through the work of the Bureau of Mines and of Dr. Fink of Columbia University, methods have been devised for concentrating low-grade manganese ores and for producing from these metallic manganese of high purity by electrolysis. It is hoped that the development of cheap water power in the far Northwest may make the manganese deposits of that region a real industrial source of this much-needed metal.

The metals. Neither of these metals is used as a pure metal, though both can be prepared by reduction of their oxides by aluminum (p. 544) or by electrolysis of their salts. Pure chromium is *plated* on other metals (Fig. 376) from baths containing chromic acid together with small concentrations of sulfate or phosphate ions. To secure a good durable plating on iron, the iron is first plated with copper, then with nickel, and finally with chromium. Pure chromium is a very hard, brilliant metal, little affected by air or water, and of melting point about that of iron. Manganese resembles iron in general physical properties but has a lower melting point (1260°).

Apart from chromium plating, both metals find their greatest use in steel metallurgy. It takes about 15 lb of manganese to make a ton of steel. The metals are prepared for this use in the form of high-

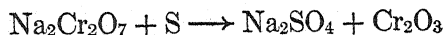
percentage iron alloys directly from ores. Chromite gives such an alloy by reduction with carbon :



Manganese ores are mixed with iron ore and the two reduced together. These alloys are called *ferrochromium* and *ferromanganese*. Their use in steel metallurgy and in steel alloys is explained on pages 641-642.

Nonferrous alloys. Both chromium and manganese are constituents of many alloys other than those of iron. Chromium forms many such alloys in various combinations with tungsten, cobalt, molybdenum, vanadium, and copper. Among these are Nichrome and Chromel (nickel and chromium), used for resistance wire in heaters (Fig. 376); and Stellite (chromium, cobalt, tungsten), used for making very hard cutting tools and for its rust-resisting properties. In small percentages manganese is a constituent of such alloys as manganese bronze (copper and manganese), used in propeller blades for ships, and Manganin (copper, nickel, manganese) used for wire in standard resistance boxes. Some varieties of brass contain manganese.

Oxides and hydroxides of the metals. Both chromium and manganese form oxides corresponding to each of their valences, and in addition manganese forms the double oxide Mn_3O_4 , similar to magnetic oxide of iron (Fe_3O_4). Both metals form hydroxides corresponding to oxides in which the valences of the metals are 2, 3, or 4. Manganese dioxide, MnO_2 (pyrolusite), in which the metal is quadrivalent, is the common oxide of manganese, while chromic oxide, Cr_2O_3 , is the stable oxide of chromium. It is a bright-green solid, used as a pigment in paints (chrome green), and is made by the reduction of sodium dichromate, $\text{Na}_2\text{Cr}_2\text{O}_7$:



Chromite, containing Cr_2O_3 , is used in making heat-resisting bricks for furnace linings.

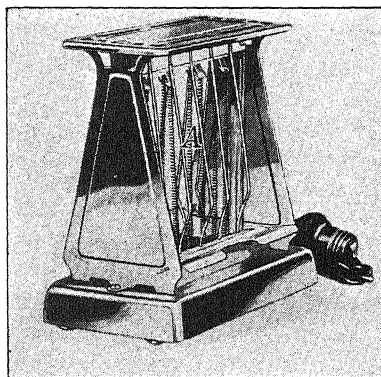
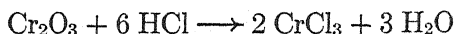


Fig. 376. A Chromium-Plated Electric Toaster

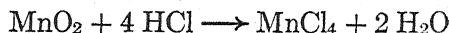
The resistance wire A is an alloy of chromium

Salts of chromium and manganese as base-forming elements. In all common chromium salts chromium acts as a trivalent base and gives salts that are similar to ferric salts in formulas. Crystallized from water, they are all hydrated and are green or violet in color. The deep-violet crystals of potassium chrome alum, $\text{KCr}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$, are especially well formed. The simple salts are made by the action of acids on chromium oxide or hydroxide,

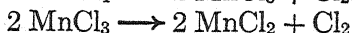
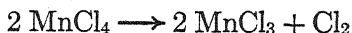


or by the action of acids, together with reducing agents, on compounds of higher chromium valence, as will be described in connection with chromates and dichromates.

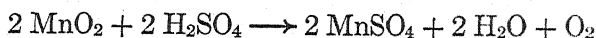
Manganese dioxide, treated with acids, undergoes reduction and gives salts of bivalent manganese. With hydrochloric acid the primary action seems to be one of ordinary double decomposition:



This is followed by successive reductions of the tetrachloride, with evolution of chlorine:

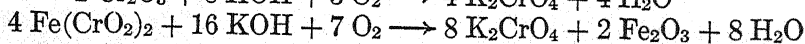
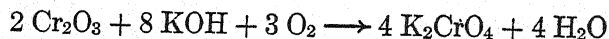


With concentrated sulfuric acid, manganese sulfate, MnSO_4 , is formed and oxygen is evolved:

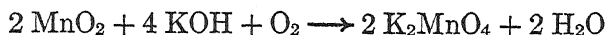


In all common salts manganese is bivalent. The soluble ones are always hydrated, such as $\text{MnCl}_2 \cdot 4 \text{H}_2\text{O}$ and $\text{MnSO}_4 \cdot 4 \text{H}_2\text{O}$; but the degree of hydration depends on the temperature of crystallization. Sulfates with 5 or 7 molecules of water are easily obtained. All the soluble salts are rose-pink in color; the insoluble ones, such as the carbonate, MnCO_3 , and the sulfide, MnS , are nearly white.

Preparation of chromates and manganates. When a compound of chromium or of manganese is fused with an alkali (or an alkaline carbonate), and with free access of air or with an oxidizing agent, the metals advance to a valence of 6 and form salts of *acids*. These acids, H_2CrO_4 and H_2MnO_4 , are similar to sulfuric acid in formula, and their salts are called *chromates* and *manganates*. With chromium compounds the reactions may be illustrated by the equations



Under similar conditions pyrolusite (MnO_2) yields potassium manganate:

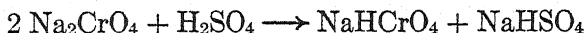


The chromates and manganates. Potassium chromate, K_2CrO_4 , is a well-crystallized lemon-yellow salt; and sodium chromate, $\text{Na}_2\text{CrO}_4 \cdot 10 \text{H}_2\text{O}$, is a very soluble yellow salt made by substituting sodium hydroxide (or carbonate) in the reactions just described. Ammonium chromate, $(\text{NH}_4)_2\text{CrO}_4$, is made by treating chromic acid with a large excess of ammonium hydroxide. It is hydrolyzed by water to form ammonium dichromate, $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$.

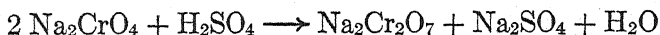
Most other chromates are insoluble in water or nearly so. They are yellow, red, or brown in color, and some of them are used as paint pigments. Among these are barium chromate, BaCrO_4 , zinc chromate, ZnCrO_4 , and lead chromate, PbCrO_4 (chrome yellow). Silver chromate, Ag_2CrO_4 , is brick-red in color.

In contrast with the chromates, the manganates are very unstable and exist only in strongly alkaline solutions. From such solutions dark-green crystals of potassium manganate, K_2MnO_4 , and sodium manganate, $\text{Na}_2\text{MnO}_4 \cdot 10 \text{H}_2\text{O}$, have been prepared with difficulty. These two salts are isomorphous with the corresponding sulfates.

The dichromates. If we treat a solution of a chromate with sulfuric acid, we might expect to find an *acid* chromate crystallizing from the solution, for this is the way we get acid sulfates and acid phosphates:

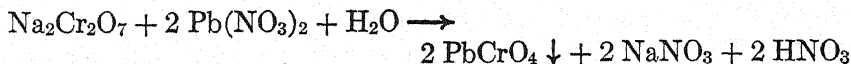


If such a salt forms at all, it at once loses water, for we get a dichromate, $\text{Na}_2\text{Cr}_2\text{O}_7$:



Potassium dichromate, $\text{K}_2\text{Cr}_2\text{O}_7$, forms brilliant orange-red crystals of moderate solubility, while sodium dichromate, of similar color, is a very soluble, hydrated salt of the formula $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2 \text{H}_2\text{O}$. These two salts are the most familiar compounds of chromium and have many uses as oxidizing agents.

It might be thought that some dichromates would be insoluble and capable of preparation by precipitation; but such double decomposition reactions always lead to the precipitation of a *chromate*, not a dichromate:



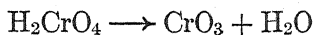
The permanganates. The valence of 7 rather than 6 is the natural maximum valence of manganese; and as we have seen, manganates are stable only in strongly alkaline solutions. If the excess of alkali is neutralized, even by very weak acids, the manganates undergo an interesting hydrolysis whereby a part of the manganese is oxidized to its more stable valence of 7 at the expense of another part, which is reduced to a valence of 4:



The resulting potassium permanganate, KMnO_4 , is a salt of permanganic acid, HMnO_4 . It forms deep-purple soluble crystals, and even its dilute solutions are intensely purple in color. Sodium permanganate crystallizes with difficulty to form hydrated crystals, $\text{NaMnO}_4 \cdot 3 \text{H}_2\text{O}$. Its solution is used as a disinfectant. All permanganates, like the corresponding perchlorates, are soluble in water.

Permanganates, as well as free permanganic acid, can be prepared by electrolysis of solutions of the manganate under conditions such that the manganate ions (MnO_4^{--}) are oxidized to permanganate ions (MnO_4^-) at the anode of a suitable cell.

Chromic acid and permanganic acid. These acids are both obtainable from their salts *in dilute solutions*, but neither acid can be crystallized. When concentrated, chromic acid deposits deep purple-red crystals of chromic anhydride, CrO_3 ,

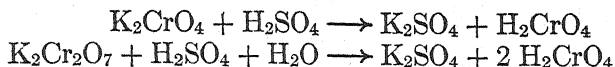


while permanganic acid decomposes into lower oxides of manganese, free oxygen, and water. By carefully treating crystals of potassium permanganate with concentrated sulfuric acid, permanganic anhydride, Mn_2O_7 , can be obtained as a highly explosive, greenish, oily liquid.

Oxidizing action of chromates, dichromates, and permanganates. Chromates, dichromates, and permanganates are strong oxidizing agents, and the reason for this is not difficult to understand. Chromium and manganese are both essentially *metals*, and as such tend to act as simple cations of salts. Under powerful oxidizing conditions they have been pushed into higher valences to form highly oxidized compounds which are unstable in character. Consequently, in the presence of even mild reducing agents, the chromate and permanganate anions tend to lose their loads of oxygen and pass back to the more natural metallic cations. This reduction of chromates or permanganates may take place either in acid solution, in alkaline solution, or in a neutral one.

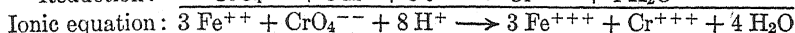
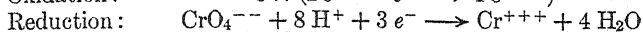
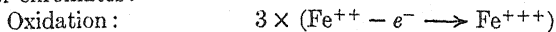
Oxidizing action of chromates and dichromates in acid solution.

If we add sulfuric acid to a solution of a chromate or a dichromate, the weak chromic acid is set free:

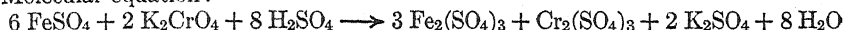


But the chromate anions tend to pass into the state of trivalent chromium ions to form a chromium salt and in this way become strong oxidizing agents. If an oxidizable material like ferrous sulfate is present, a reaction takes place which may be represented as follows:

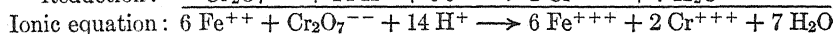
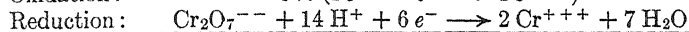
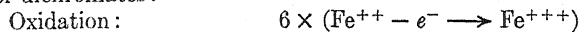
For chromates:



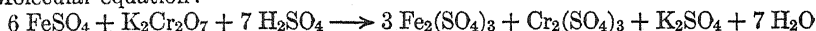
Molecular equation:



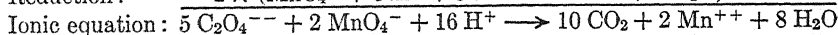
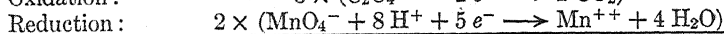
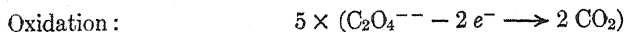
For dichromates:



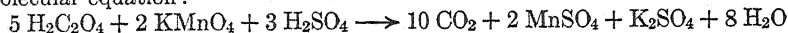
Molecular equation:



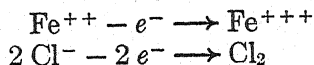
Oxidizing action of permanganates in acid solution. As with the chromium in chromates, the manganese in permanganates tends to pass back to the state of a simple metallic ion, which in this case is the bivalent ion Mn^{++} . In a solution containing potassium permanganate, sulfuric acid, and an oxidizable substance like oxalic acid, $\text{H}_2\text{C}_2\text{O}_4$, the equations become



Molecular equation:

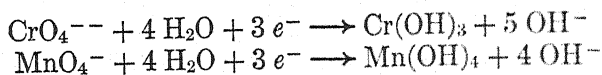


Similar complete equations may be obtained by combining the equation for the reduction of the permanganate ion with other oxidation equations, such as

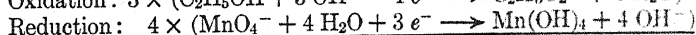
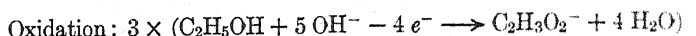


A permanganate is intensely colored in solution, while the products formed both from the permanganate and from the oxidation of the reducing agent have very little color as a rule. The end-point of a reaction in which a permanganate is used as an oxidizing agent is sharply marked by the disappearance of color, which makes potassium permanganate an invaluable reagent in chemical analysis.

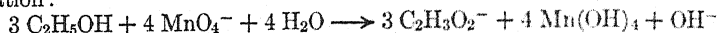
Oxidizing action of chromates and permanganates in neutral or alkaline solution. In the presence of an oxidizable substance and in a neutral or alkaline solution, the chromium of chromates (and dichromates) and the manganese of permanganates do not yield salts of simple metallic ions, but instead the hydroxides of these ions:



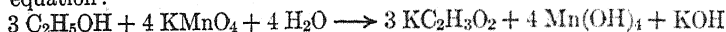
For example, in dilute solution alcohol is oxidized to acetates by potassium permanganate:



Ionic equation:



Molecular equation:



In general, chromates and permanganates are not as energetic oxidizing agents in neutral solutions as in acid ones.

Masurium and rhenium. Two new elements of the manganese family (of atomic numbers 43 and 75) were discovered in 1925 after prolonged search by Walter Noddack and Ida Tacke at Berlin. The elements were first found by Moseley's X-ray method in ores of tantalum and later in those of molybdenum and manganese. They were named *masurium* and *rhenium* in memory of provinces of Germany. Masurium has never been isolated in a pure state, but rhenium is available to about the same extent as such a rare element as gallium. In chemical conduct rhenium closely resembles manganese. Its density is 21.1, and its melting point above 3200°. About 300 lb are produced annually.

METALLO-ACID ELEMENTS USED CHIEFLY AS METALS OR ALLOYS

General. Of the remaining six elements in the table at the beginning of this chapter, two, vanadium and uranium, form salts in their lower valences and acids in their higher ones, just as do

chromium and manganese. The others, columbium, tantalum, molybdenum, and tungsten, have almost no salt-forming ability as positive ions, but in their higher valences they all form acids. All six form a variety of oxides and compounds with the halogen elements, especially with fluorine and chlorine. All six have high melting points and densities, together with other properties that characterize most heavy metals. All are used chiefly in the form of free metals or alloys, and their compounds do not require special descriptions. All are difficult to prepare in pure form.

Vanadium, columbium, tantalum. These three elements constitute family A, Group V, in the periodic table, and in their properties show many of the gradations we expect to find in a periodic family.

Vanadium. Vanadium was first described as a new element by Sefstrom in 1830, and named in honor of Vanadis, the Scandinavian goddess of fortune. It is widely distributed in nature but rarely in rich deposits. In the United States the deposits are in Colorado, Arizona, and Utah, and the chief ore is *carnotite* — a complex mineral of the formula $K_2O \cdot 2 UO_3 \cdot V_2O_5 \cdot 3 H_2O$. The chief foreign producing countries are Mexico, Peru, and Africa. The Peruvian ore is *patronite*, a complex sulfide, which is mined in the very high Andes Mountains. This mineral seems to be the residue of the complete evaporation of asphalt; and it is of interest that the ashes of nearly all anthracite and of petroleum contain vanadium oxide, sometimes in large percentages.

The metal. Metallic vanadium is difficult to prepare and has no special uses. It is very hard, rather brittle, and has a brilliant luster. By reducing a mixture of the oxides of iron and vanadium, an alloy called *ferrovanadium* is obtained, which usually contains from 25 to 50 per cent vanadium. It is important in the manufacture of vanadium steel, which is the chief use of vanadium. Some vanadium compounds are employed as catalysts in the manufacture of dyes and especially in the contact process for sulfuric acid (p. 363). For the latter purpose vanadium oxide (V_2O_5) is interspersed throughout some inert porous material, and the product so formed is often called "vanadium mass."

Columbium and tantalum. The history of these two elements is an interesting story of confused identity. At some early date Governor John Winthrop sent a specimen of a new mineral found in Connecticut to England, where it became lodged in the British Museum. The mineral was named *columbite* in honor of America. In 1801 the English chemist Hatchett examined this mineral and

from it isolated what was undoubtedly the oxide of a new element, which he named *columbium*. A few years later the Swedish chemist Ekeberg examined a Swedish mineral (now called *tantalite*) and found an oxide of a metal which he named *tantalum* (from the Greek mythological figure Tantalus). Later chemists considered these two oxides to be identical, though the German Heinrich Rose maintained they were different. He retained the name tantalum for the oxide of Ekeberg, but gave the name *niobium* to Hatchett's columbium (Niobe was the daughter of Tantalus). Finally, after some forty years of uncertainty, the French chemist Marignac prepared pure specimens of tantalic and niobic acids and demonstrated their different properties. In some countries Hatchett's metal is called niobium, but in America it is called columbium.

The metals themselves proved to be very difficult of reduction. Moissan prepared some impure specimens in his electric furnace, but the first really pure small specimen of columbium was produced in Germany in 1906. The first production of any quantity of both these metals was exhibited by the American chemist Balke in 1929.

The ores of columbium and tantalum. These two metals are found almost wholly as salts of columbic acid, HCbO_3 , and tantalic acid, HTaO_3 ; and small percentages of such salts are present in a great variety of minerals. The only minerals adapted to the preparation of the metals themselves are *columbite* and *tantalite*. Both these are mixtures of the iron or manganese salts of both acids in varying proportions. With larger percentages of columbic acid the mineral is called columbite; if tantalum predominates, it is tantalite. If a mineral contains the one acid, it almost always contains the other. They are twin metals; always together and very difficult to separate. Tantalite is sought for the production of metallic tantalum, and is found chiefly in Australia and South Dakota; while columbite, nearly free from tantalum, comes from Africa and is used in making ferrocolumbium. In either case the ores are not rich and must be concentrated. About $2\frac{1}{2}$ tons of ore must be mined, concentrated, and processed to produce one pound of tantalum.

Metallurgy. The metallurgy of these elements is strikingly different from that of any others we have considered. By a number of tedious steps the two metals are brought into the form of double fluorides, which differ in formulas, K_2TaF_7 and K_2CbOF_5 . Fortunately these compounds differ somewhat in solubility and can be separated by fractional crystallization. The chemically pure salts are then melted and electrolyzed to yield metallic powders which cannot be melted in the usual way because of the extremely high

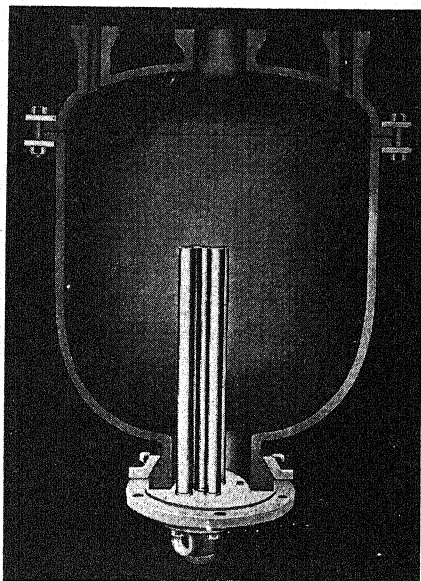
melting points of the metals. The powders are compressed into rods by great pressure, and, by the heat generated in the rods by their resistance to an electric current, the metallic particles partially weld together. By alternate heating and hammering of the rods a finished metal is produced.

In 1936 a large deposit of columbite, $\text{Fe}(\text{CbO}_3)_2$, low in tantalum, was found in Africa. From this ore *ferrocolumbium* is made (like ferrochromium) by reducing the treated mineral with carbon in an electric furnace. The product may contain over half its weight of columbium. Added to stainless steel, columbium increases the resistance to corrosion of the steel and improves its welding properties. It is said that nearly 500,000 lb of columbium is used annually for this purpose.

Properties of the metals. The two metals resemble platinum or polished iron in appearance. Tantalum has a very high melting point, which among metals is second only to that of tungsten; columbium melts at a much lower temperature. Both metals are highly malleable and ductile. In hardness unannealed tantalum is comparable to cold-rolled steel, and the annealed metal to mild steel.

At ordinary temperatures tantalum resists corrosion by nearly all acid and salt solutions. It is most easily attacked by alkalies and by such salts as produce alkalies by hydrolysis. Fluorine attacks it, and it absorbs hydrogen. Columbium is similar to tantalum in many respects, but corrodes more easily and absorbs hydrogen to a greater extent.

Uses of tantalum. The uses of tantalum depend on its high melting point, hardness, malleability, resistance to corrosion, and its very great heat conductance. These properties lead to many varieties of laboratory articles, to electrodes in radio tubes and in rectifiers (the Balkite rectifier), to nozzles and spinnerets subject to great



Fansteel Metallurgical Corporation

FIG. 377. Vessel for Heating Corrosive Liquids, Equipped with Tantalum-Tube Heaters

abrasion, to surgical instruments, and especially to stirrers and steam heaters for corrosive liquids, such as acids and salts (Fig. 377). Columbium can be used for many of these same purposes.

The oxides of tantalum and columbium, heated with carbon in an electric furnace, yield carbides of great hardness. They can be added to steel to increase its hardness for making cutting tools, or steel tools can be tipped with these carbides.

Molybdenum, tungsten, uranium. These three elements follow chromium in family A, Group VI, of the periodic table. All three of the metals, together with chromium, came to the knowledge of chemists in the last two decades of the eighteenth century in the form of definite compounds, but it is within modern times that they have become important as metals.

Historical. In 1778 the great Swedish chemist Scheele (Fig. 189) became interested in a mineral called *molybdenite*, which had long been confused with graphite. He showed these minerals to be entirely different, and from the molybdenite he isolated an acid oxide which he named molybdic acid; for in those days all acids were thought to be oxides.

Three years later he examined a very heavy, white Swedish mineral, then called tungsten, or heavy stone, now named *scheelite* (CaWO_4); and from this he isolated a second acid oxide (WO_3), which he named tungstic acid. A little later this same acid was found in a mineral occurring in Cornish tin mines, which miners called *wolfram*. This led to a confusion of names. The name tungsten is retained for the element in most countries, but the symbol W is universally used to designate it.

In 1789 the German chemist Klaproth investigated a mineral called *pitchblende* and proved that the oxide of a new element could be obtained from it. He named the metallic base of this oxide *uranium* in honor of the planet newly discovered by Herschel (in 1781).

Ores of molybdenum and tungsten. These two metals (and their compounds) are today produced almost entirely from the minerals in which they were discovered — molybdenum from molybdenite, MoS_2 , and tungsten from scheelite, CaWO_4 , but more largely from wolframite. The latter is a salt of tungstic acid, H_2WO_4 , in which the bases consist of iron and manganese in variable proportions, so that the formula is written $(\text{Fe}, \text{Mn})\text{WO}_4$. Colorado has by far the largest deposit of molybdenite, with smaller ones in California, Canada, and other places. Ores of tungsten have come largely from China and Burma. In the United States wolframite is found in Nevada and Colorado; and scheelite, in California.

Metallurgy of the metals. Fortunately it is not necessary to extract these two metals from one mineral (as it was with columbium

and tantalum), and it is relatively easy by roasting and fusion of ores to work the two metals into the form of the oxides MoO_3 and WO_3 . The metals both melt at exceedingly high temperatures; and for their production, especially for tungsten, it is necessary to resort to "powder metallurgy," as was described in connection with tantalum. The heated oxide is reduced to metallic powder in a current of hydrogen, and the powder is worked into continuous metal, as with tantalum. Molybdic oxide can also be reduced by aluminum.

Properties and uses of the metals. In their physical properties the two metals resemble each other closely, though molybdenum melts about 750° lower than tungsten and is approximately half as heavy. Both metals tend to be crystalline and very hard and brittle. By prolonged mechanical treatment they both become very malleable and capable of being drawn into wire much smaller than a human hair. Tungsten is a much better electrical conductor than molybdenum, and the tungsten filament in an electric lamp must be drawn very fine and looped in many loops to have enough resistance to bring the wire to a white heat.

The properties of these metals make them exceedingly useful for all sorts of electrical purposes — electrodes, grids, supports in radio and thermionic tubes, electrodes for neon tubes, targets for X-ray tubes, filaments for electric lamps, and contact points for electric switches and automobile distributors. Molybdenum is used chiefly for supporting wires and parts that are not too highly heated, for it is much cheaper than tungsten. Its resistance is greater than that of tungsten, and molybdenum wire is used as the heating unit in some types of electric furnaces. Both metals oxidize easily at higher temperatures and when so used must be protected from air.

A very large use for the metals is in making steel alloys, as described under steel. For this purpose tungsten is prepared as ferro-tungsten by the reduction of wolframite with carbon; and ferromolybdenum, by reduction of a mixture of iron oxide and molybdic oxide. Both metals are used in a number of nonferrous alloys as well, chiefly those of chromium, nickel, and cobalt.

Compounds of molybdenum and tungsten. Of these the carbides of tungsten are the most interesting, especially the one of the formula WC_2 . It is a crystalline material approaching close to the diamond in hardness. It has been found possible to embed these fine crystals in suitable binders, especially in metallic cobalt, and so obtain a cutting tool that surpasses all others for many uses. *Carboloy* is the best-known trade name for this material, and a Carboloy lathe tool will cut threads on a hard-glass tube (Fig. 378) and can be used

to machine hard rubber. A carbide of tantalum is used as a cutting tool under the trade name Tantaloy. The carbides of these metals can also be used as abrasives for grinding hard metal parts.

There are a great many compounds of both molybdenum and tungsten, but few have important useful applications. Both elements form a few simple salts corresponding to chromates, such as K_2MoO_4 and Na_2WO_4 ; but for the most part the molybdates and tungstates are much more complex and are derived from condensed acids (p. 426). For example, ordinary ammonium molybdate has the formula $(NH_4)_6Mo_7O_{24} \cdot 4 H_2O$. Sodium tungstate, Na_2WO_4 , has some use as a fire-resisting finish on cloth and as a mordant in dyeing. Compounds of molybdenum are used for blue colors in china-painting, for coloring leather, and in dyeing.

Uranium. Uranium is found most abundantly as pitchblende, U_3O_8 , and is of interest chiefly as the element of highest atomic

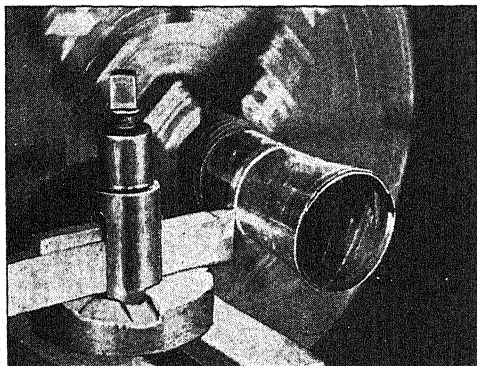


FIG. 378. Cutting a Glass Tube with a Carbide Lathe Tool

weight and the one from which radium is derived (p. 220). The metal is difficult to prepare in pure condition, and no important uses have been found for it. It is said to resemble nickel in appearance. As an acid-forming element it is similar to chromium, in that it forms salts of the formulas M_2UO_4 and $M_2U_2O_7$, but ordinarily it plays the part of a base-forming element. In this

capacity it forms a great variety of salts, the best known of which are a series in which the radical UO_2 , known as *uranyl*, acts as a bivalent metal. Examples of these salts are uranyl nitrate ($UO_2(NO_3)_2 \cdot 6 H_2O$) and uranyl acetate ($UO_2(C_2H_3O_2)_2 \cdot 2 H_2O$). The oxides of uranium have long been used in making greenish-yellow fluorescent glass and in glazes.

Bombardment of uranium by neutrons. The results of the bombardment of some atomic nuclei by neutrons have already been described, but similar bombardment of uranium has led to surprising results. The nucleus, struck by slow-moving neutrons, seems to break up into nuclei of a number of large atoms, such as barium and xenon, with the liberation of an enormous amount of energy. By positive-ray analysis (p. 216) Dr. Nier of the Uni-

versity of Minnesota succeeded in isolating the isotope U-235 and depositing a minute quantity of it on platinum plates. Bombardment of these plates in the cyclotron at Columbia University proved that this isotope goes to pieces under neutron bombardment, and not only releases energy but slow-moving neutrons as well which are able to start similar decompositions in near-by U-235 nuclei. So once started, the effect should be cumulative.

Dr. Nier estimates that 1 lb of U-235 would generate as much force as 2,000,000 lb of coal, but the greatest weight of U-235 which he has been able to isolate is less than $\frac{1}{100,000,000}$ oz. In natural uranium the ratio of U-235 to U-238 is about 1 to 139, and there is also present the third isotope, 234. Whether U-235 can be separated from its isotopes industrially and how far the energy of the isotope can be utilized are questions that are fascinating scientists in all countries.

Questions

1. For what reason are the eight elements of this chapter grouped together?
2. Why describe chromium and manganese apart from the other six elements?
3. What distinction can you make between the metallo-elements and those metals whose hydroxides are amphoteric?
4. What six important nonferrous alloys can you name other than those mentioned in this chapter?
5. What chemical principle underlies the production of chromates and manganates from their ores?
6. Why is barium chromate (BaCrO_4) precipitated from an acid solution of sodium dichromate rather than barium dichromate?
7. Temperatures much above the melting point of tantalum or tungsten can be attained in an electric furnace. Why not melt the powder of these metals into a solid ingot in such a furnace?
8. In the equations on page 715 (a) what is oxidized; (b) what is reduced; (c) what acts as an oxidizing agent; (d) what acts as a reducing agent?
9. In hydrochloric acid solution potassium permanganate oxidizes ferrous chloride to ferric chloride. What is the equation?
10. In acid solution sodium dichromate oxidizes methyl alcohol (CH_3OH) to formaldehyde (CH_2O). What is the equation?

Problems

1. What weight of potassium permanganate can be prepared from 100 g of pure pyrolusite by first preparing the manganate and then treating its solution with nitric acid?
2. In acid solution which salt has the greater oxidizing value per 100 g and by what per cent, potassium permanganate or sodium dichromate?
3. (a) What weight of potassium permanganate will be required for the oxidation in alkaline solution of 1 kg of 95 per cent alcohol to acetic acid? (b) How could you recover the acetic acid?
4. What weight of (pure) hematite and chromite must be mixed and reduced to obtain 200 lb of ferrochromium containing 50 per cent chromium and 5 per cent carbon?
5. A sample of iron ore weighing 0.3 g was dissolved in sulfuric acid, and the resulting ferrous sulfate was oxidized to ferric sulfate by potassium permanganate. The oxidation required 28 cc of a solution of the permanganate prepared by dissolving 3.16 g of the permanganate in 1 l of water. Calculate the percentage of iron that was present in the ore.

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- KILLEFER. "Chromium Plating," *Industrial and Engineering Chemistry*, Vol. XIX, pp. 773-776.
- LAURENCE. "The Atom Gives Up," *The Saturday Evening Post*, September 7, 1940, p. 12. Very interesting.
- LIND. "Chemistry within the Atom," *Science*, Vol. 92, pp. 227-231.
- WEEKS. *The Discovery of the Elements*. Read of the discovery of the elements treated in this chapter (consult index for pages).
- The magazine *Fortune*, Vol. XIV, No. 4, p. 105, gives an interesting account of molybdenum.
- Consult the Minerals Yearbook for information concerning the production of the metals referred to in this chapter.

CHAPTER 40

Gold and the Platinum Family

ELEMENT AND SYMBOL	ATOMIC WEIGHT	ATOMIC NUMBER	DENSITY	MELTING POINT	ELECTRONS IN SHELLS
Ruthenium (Ru)	101.7	44	12.2	2450° (?)	2:8:18:14:2
Rhodium (Rh)	102.91	45	12.5	1955°	2:8:18:15:2
Palladium (Pd)	106.7	46	12.0	1555°	2:8:18:16:2
Osmium (Os)	190.2	76	22.48	2700° (?)	2:8:18:32:14:2
Iridium (Ir)	193.1	77	22.4	2350° (?)	2:8:18:32:15:2
Platinum (Pt)	195.23	78	21.45	1755°	2:8:18:32:16:2
Gold (Au)	197.2	79	19.3	1063°	2:8:18:32:18:1

General. In the periodic arrangement gold is placed with copper and silver in Group I, but it is much more closely related to the platinum metals and will be considered along with them.

Group VIII in the periodic table is made up of three sets of elements, each consisting of three members. The first set, comprising iron, cobalt, and nickel, has been described in a previous chapter. The six members of the other two sets, including ruthenium, rhodium, palladium (with atomic weights of approximately 100), and osmium, iridium, and platinum (with atomic weights lying near the value 195), are very closely related to each other and are known collectively as the *platinum metals*.

GOLD

Occurrence. From the earliest times gold has been known as a precious metal. It was called *aurum* by the Romans, and from this name the symbol Au is derived. For the most part it is found as metallic gold, either embedded in quartz veins or as grains or large nuggets in the heavy sands resulting from the weathering of quartz rock. Usually the native gold contains small quantities of other metals, such as silver, copper, and lead. In compound form it occurs in a number of minerals, nearly all of which contain tellurium together with silver and copper. A little gold telluride is apparently dissolved in the sulfides of many other metals, such as those of copper, lead, and silver; and gold is obtained as a by-product in the refining of these metals. South Africa produces approximately one

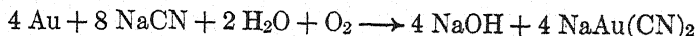
third of the world's output of gold; Canada produces about 14 per cent and the United States a little less. The production in the United States and its possessions, in recent years, has risen sharply to as much as 5,000,000 troy ounces annually, with Alaska, California, South Dakota, and Colorado as the leading producers.

Properties. Gold is a yellow metal which melts at about the same temperature as copper and boils at approximately 2500°. It is about as soft as silver, is a good conductor of electricity, and is the most ductile and malleable of the metals. It forms alloys with most metals, and its uses are too familiar to require description. In a pure condition gold is too soft to be used for jewelry and coinage, and for such purposes it is always alloyed with copper or silver. The fineness of gold is usually expressed in terms of carats, 24-carat gold being pure, while 18-carat (75 per cent) is the grade used for the best jewelry. For coinage a 90 per cent alloy is used. It has been estimated that if all the monetary gold in the world were to be cast into one large cube, the cube would have an edge length of somewhat more than 30 ft and would weigh in the neighborhood of 20,000 tons.

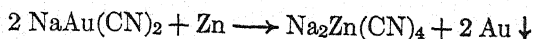
Mining and extraction. Native gold is recovered in crude form by *placer* mining. The sand containing the gold is shaken or stirred in troughs of running water, called *sluices*. This sweeps away the sand but allows the heavier gold to sink to the bottom of the sluice. Sometimes the sand containing the gold is washed away from its natural location into the sluices by powerful jets of water. This is called *hydraulic* mining. In *vein* mining the gold-bearing quartz is stamped into fine powder in stamping mills, and the gold is extracted by a number of processes, two of which are the following:

1. **Amalgamation process.** In the amalgamation process the powder containing the gold is washed over a series of copper plates whose surfaces have been amalgamated with mercury. The gold sticks to the mercury or alloys with it, and after a time the gold and mercury are scraped off and the mixture is distilled. The mercury distills off, and the gold is left in the retort, ready for refining.

2. **Cyanide process.** This process depends upon the fact that gold is soluble in a solution of sodium cyanide in the presence of the oxygen of the air. The powder from the stamping mills is treated with a very dilute sodium cyanide solution which dissolves the gold:



From this solution the gold can be obtained by electrolysis or by precipitation with metallic zinc:



Refining of gold. Gold is refined by four general methods :

1. **Electrolysis.** When gold is dissolved in a solution of sodium cyanide and the solution electrolyzed, the gold is deposited in very pure condition on the cathode.

2. **Cupellation.** When the gold is alloyed with easily oxidizable metals, such as copper or lead, it may be refined by cupellation. The alloy is fused with an oxidizing flame on a shallow hearth made of bone ash, which substance has the property of absorbing metallic oxides but not the gold. Any silver which may be present remains alloyed with the gold.

3. **Parting with sulfuric acid.** Gold may be separated from silver, as well as from many other metals, by heating the alloy with concentrated sulfuric acid. This dissolves the silver, while the gold is not attacked. Sometimes nitric acid is used instead of sulfuric acid.

4. **Action of chlorine on molten alloy.** The crude alloy is melted, and chlorine gas is bubbled through it. The silver and copper are converted into chlorides (solids) and are skimmed off. The residual gold is then put into solution and separated by electrolysis.

Chemical conduct. Gold is not attacked by any one of the common acids. It is easily dissolved by solutions containing free chlorine or bromine, by aqua regia, and by solutions of sodium cyanide in the presence of air. Fused alkalies also corrode the metal, with the formation of aurates of the general type KAuO_2 .

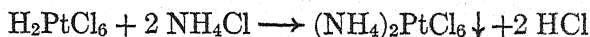
In its compounds gold nearly always acts as a trivalent element. Auric hydroxide $(\text{Au}(\text{OH})_3)$ yields two series of compounds. One is represented by such salts as the chloride, AuCl_3 , while the other consists of aurates, such as potassium aurate (KAuO_2) .

Complex compounds. The great majority of the compounds of gold are complex compounds, such as cyanides and ammonia derivatives. Among the most important is *chloroauric acid* (HAuCl_4) , formed by dissolving gold in aqua regia. The sodium salt $(\text{NaAuCl}_4 \cdot 2\text{H}_2\text{O})$ is used as a toning reagent in photography. The cyanides $\text{KAu}(\text{CN})_2$ and $\text{KAu}(\text{CN})_4$ are used as electrolytes in gold-plating. One of the most characteristic reactions of gold compounds is the production of a purple precipitate known as the *purple of Cassius*, when a solution containing stannous chloride and stannic acid is warmed with a very dilute solution of a gold salt. The gold salt is reduced by the stannous chloride, and purple colloidal gold is precipitated along with colloidal stannic acid.

PLATINUM

History and occurrence. The element *platinum* owes its name to the Spanish word *platina*, which is a diminutive of the word *plata*, "silver." It was introduced into Europe through the Spanish conquests of Peru and Mexico. The first large quantity reached England in 1740 from Jamaica, and in 1750 it was first described with some care by Brownrigg. Platinum occurs in nature alloyed with the various metals belonging to the gold and platinum family, as well as with other metals. Like gold, it occurs in heavy sands, associated with magnetite, zircon, diamond, and quartz, and constitutes from 50 to 80 per cent of the crude alloy. A single well-defined mineral compound is known, namely, *sperrylite* (PtAs_2). Formerly nearly all the world's supply of platinum came from the Ural Mountains in Russia. In recent years Canada has been the chief producer, owing to the recovery of platinum from the electrolytic mud of the copper and nickel refineries at Sudbury, Ontario. South Africa, Colombia, and the United States (Alaska, California, and Oregon) are important producers.

Preparation. Native platinum is usually alloyed with gold and the platinum metals in flakes, scales, or small nuggets. To separate the platinum the alloy is dissolved in aqua regia, which converts the platinum into chloroplatinic acid (H_2PtCl_6). Ammonium chloride is then added, which precipitates the platinum as insoluble ammonium chloroplatinate :



Some iridium is also precipitated as a similar compound. On ignition the chloroplatinate is decomposed, leaving the platinum as a spongy metallic mass, which is melted in an electric furnace and rolled or hammered into the desired shape.

Properties. Platinum is a grayish-white metal which is very malleable and ductile, and is harder than gold. In finely divided form it adsorbs gases and occludes hydrogen. A jet of hydrogen or coal gas directed upon spongy platinum, in air, is at once ignited. Under ordinary conditions it is not attacked by the common acids, though hot concentrated sulfuric acid slowly dissolves it. It is quite permanent in the air, and neither oxygen nor water vapor attacks it even at red heat. Free chlorine dissolves it, forming platinum tetrachloride (PtCl_4). Aqua regia converts it into *chloroplatinic acid* (H_2PtCl_6). Fused alkalis corrode it, forming platinates, especially in the presence of oxidizing agents such as nitrates. It alloys readily

with many easily reducible metals, and is therefore attacked or dissolved when heated with compounds of such metals together with a reducing agent. Since hydrogen gas readily passes through sheet platinum when the latter is hot, it is not safe to heat, in a gas flame, any easily reducible oxide in a platinum crucible.

Platinum as a catalytic agent. Platinum is remarkable for its property of acting as a catalytic agent in a large number of chemical reactions, and mention has been made of this use of the metal in connection with the manufacture of sulfuric acid (p. 362). The catalyst support, generally some porous or fibrous substance, such as asbestos, is soaked in a solution of chloroplatinic acid and then ignited. The platinum compound is decomposed, and the platinum deposited in very finely divided form. Asbestos prepared in this way is called *platinized asbestos*. For some reactions, as in the oxidation of ammonia by air (p. 385), the platinum is used in the form of a finely woven gauze. The catalytic action seems to be in part connected with the property of adsorbing gases and rendering them nascent.

Applications. Platinum is more costly than gold, but its value is subject to wide fluctuations. Its applications are therefore limited. Its greatest use is in the making of jewelry; more than one half of the supply is used for this purpose. Next in order comes its use for chemical and dental purposes. Smaller amounts are used (1) in the construction of electrical apparatus, (2) as a catalyst in certain industrial processes, and (3) for making crucibles and evaporating dishes used in scientific laboratories (Fig. 379).

Platinum substitutes. To conserve the limited supply of platinum, efforts have been made to provide substitutes for some of its uses. Tungsten is taking its place for many purposes, especially for electrical spark contacts; tantalum can replace it in making many scientific instruments; wires of nickel-iron coated with copper are now used as lead-in wires in incandescent lamps; electrical-resistance heaters are made of alloys of nickel and chromium; quartz dishes are substituted for platinum in the industries; and a variety of alloys such as *Palau*, an alloy of palladium and gold, have been proposed for use in small laboratory utensils, though none have any very wide application.

Compounds of platinum. Like tin, platinum acts either as a bivalent or as a quadrivalent element, and the hydroxide corresponding to each valence can act either as an acid or as a base. Some trivalent compounds are also known. In general, the oxygen derivatives of platinum, including the oxygen acids, as well as the platinates and platinites, are unstable and easily decomposed by heat. Its best-known compounds are its halogen derivatives, especially the

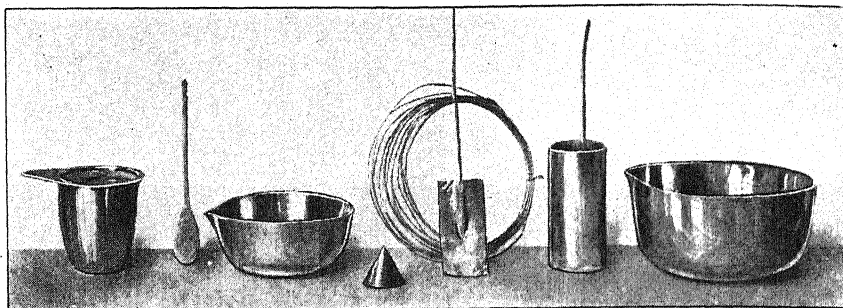
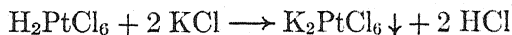


FIG. 379. *Platinum Utensils Used in Chemical Laboratories*

salts of *chloroplatinic acid* (H_2PtCl_6). This free acid, which forms reddish, deliquescent crystals of the composition $\text{H}_2\text{PtCl}_6 \cdot 6 \text{H}_2\text{O}$, is obtained by dissolving platinum in aqua regia. When added to a solution of potassium chloride, *potassium chloroplatinate* is formed as a reddish-yellow salt :



Sodium chloride and ammonium chloride act in the same way. The sodium salt, however, is soluble in dilute alcohol, while the salts of potassium and ammonium are not, and this difference in property is taken advantage of in the separation of potassium and sodium from each other.

Other platinum metals. The other platinum metals — palladium, rhodium, ruthenium, osmium, and iridium — are all gray metals and have very high melting points and densities. They are found alloyed with native platinum. In chemical conduct they are like gold and platinum. Each one forms several series of compounds, in which the valence is either 2, 3, or 4 ; each gives a variety of oxygen compounds of rather unstable character.

Palladium. Palladium is the most abundant one of the five. It is obtained from native platinum and also from the electrolytic muds in the refining of certain nickel ores, especially those at Sudbury, Canada (Fig. 358). It is a soft metal, closely resembling platinum in appearance, but of less density and of lower melting point. It is more pronouncedly basic than the others, dissolves in concentrated acids, especially in nitric acid, and forms a number of bivalent and moderately stable salts, such as the nitrate, $\text{Pd}(\text{NO}_3)_2$, and the sulfate, PdSO_4 . The metal has the remarkable property of occluding, or absorbing, a very large volume of hydrogen. This may amount to as much as 800–900 times the volume of the palladium, and an even larger volume is absorbed when an electrode is covered with the spongy

metal and is made the cathode in the electrolysis of a dilute acid solution. The hydrogen so absorbed is in a very active state, showing the reactions appropriate to its position in the electromotive series. For example, palladium thus charged with hydrogen, when dipped into a solution of copper salt, at once precipitates copper.

Palladium is used in making delicate instruments, and as a substitute for platinum in jewelry. It is not only cheaper than platinum, but only about half as dense, so that a given weight will go twice as far. It is also used as a catalyst in industrial reactions.

Rhodium. Rhodium resembles aluminum in appearance. Of all these metals, it is the most easily attacked by free chlorine, but it is exceedingly resistant to the action of acids. Its salts are rose-colored.

Ruthenium. Ruthenium is hard and brittle, and closely resembles platinum in appearance. It forms a variety of oxygen compounds, the formulas of which recall those of manganese — for example, RuO_2 , K_2RuO_4 , and KRuO_4 . It also forms a volatile oxide of the formula RuO_4 . This is produced by the oxidizing action of aqua regia, and is possibly formed by heating the metal in the air. It is a yellow compound, which melts at 25.5° .

Osmium. Of all known substances, osmium has the greatest density (22.48). It is very hard and infusible. It is acted upon by aqua regia to form an oxide (OsO_4) which resembles the corresponding oxide of ruthenium. This oxide is volatile with steam and is often present in the steam arising when solutions of crude platinum salts are boiled. It has a very irritating and unpleasant odor, and is called *osmic acid*, though it has no acid properties, nor does it form an acid with water. The name was given on account of its corrosive action, which it owes to oxidizing and not to acid properties. In acting as an oxidizing agent it deposits metallic osmium in very finely divided form, and this is a great irritant when deposited in sensitive tissues. It is used in biological laboratories as a hardening agent and as a stain in the preparation of microscopic sections.

Iridium. This element owes its name to the variety of colors seen during its chemical transformations. It is a silver-white metal, hard and brittle. It is often present in the platinum of laboratory vessels, making the latter harder and less subject to chemical corrosion. The standard meter bar preserved at Sèvres is an alloy of platinum and iridium. The residue obtained when native platinum is digested with aqua regia is essentially an alloy of iridium and osmium. It can be worked up into a very hard alloy called *iridosmine* (found also as a natural alloy), which is used as a material for pointing gold pens. It is produced in very limited quantities and is more expensive than gold.

Questions

1. What metal has (a) the greatest density; (b) the least density; (c) the highest melting point; (d) the lowest melting point; (e) the highest atomic weight; (f) the lowest atomic weight?
2. What metals are not attacked by any of the common acids?
3. (a) What is meant by 18-carat gold? (b) What advantage, if any, has 18-carat gold over 24-carat gold?
4. How could you obtain pure gold from 18-carat gold?
5. What compounds are formed by the action of aqua regia upon each of the following metals: (a) aluminum; (b) iron; (c) tin; (d) gold; (e) platinum?
6. Compare gold and platinum as to (a) density; (b) melting point; (c) appearance; (d) cost; (e) uses.
7. (a) What alloy is used for pointing gold pens? (b) Why not use pure platinum?
8. What country produces the most (a) gold; (b) platinum?
9. (a) What is the action of mercury upon gold? (b) Suggest a way of recovering the pure gold.
10. (a) What is the difference in composition between gold and fool's gold? (b) How could you distinguish between the two?

Problems

1. What weight of chloroauric acid can be prepared from 25 g of 18-carat gold?
2. (a) Calculate the per cent of gold in chloroauric acid; (b) of platinum in chloroplatinic acid.

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- WEEKS. *The Discovery of the Elements*. Read of the discovery and early history of the metals of the platinum family.

Appendix

CHEMICAL LIBRARY

The following list contains the names of the journals referred to in the Reading References, the publishers of each and their addresses; also the names of the authors of all books to which reference is made, the titles of the books, their publishers, and the date of the latest editions.

Journals

Journals published by the American Chemical Society (A.C.S.):

Journal of the American Chemical Society, published monthly by the A.C.S., Easton, Pennsylvania.

Journal of Chemical Education, published monthly by the Division of Chemical Education of the A.C.S., Easton, Pennsylvania.

Industrial and Engineering Chemistry, published monthly by the A.C.S., Easton, Pennsylvania.

News Edition, published semimonthly by the A.C.S., Easton, Pennsylvania.

Chemical and Metallurgical Engineering, published monthly by the McGraw-Hill Publishing Company, New York.

Journal of the Franklin Institute, published monthly by the Franklin Institute of the State of Pennsylvania, Lancaster, Pennsylvania.

National Geographic Magazine, published monthly by the National Geographic Society, Washington, D.C.

Science, published weekly by the Science Press, Lancaster, Pa.

Scientific American, published monthly by Munn and Co., New York.

Fortune, published monthly by Time, Inc., Chicago.

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DENSITIES AND MELTING POINTS OF SOME OF THE MORE COMMON ELEMENTS

NAME	DENSITY	MELTING POINT	NAME	DENSITY	MELTING POINT
Aluminum	2.702	660°	Mercury (liquid) . . .	13.546	- 38.87°
Antimony	6.684	630.5°	Molybdenum	10.2	2625°
Arsenic (metallic) . . .	5.7	814° ^{36 atm}	Nickel	8.90	1452°
Barium	3.5	850°	Palladium	12.0	1555°
Bismuth	9.80	271°	Phosphorus (red) . . .	2.20	590° ^{43 atm}
Boron	2.5	2300°	Phosphorus (yellow) . .	1.82	44.1°
Bromine (liquid)	3.119	- 7.2°	Platinum	21.45	1755°
Cadmium	8.6	320.9°	Potassium	0.86	62.3°
Calcium	1.55	810°	Radium	5(?)	960°(?)
Carbon (diamond)	3.51	—	Selenium (gray)	4.80	220°
Carbon (graphite)	2.26	3500°	Silicon	2.4	1420°
Chromium	7.1	1615°	Silver	10.5	960.5°
Cobalt	8.9	1480°	Sodium	0.97	97.5°
Copper	8.92	1083°	Strontium	2.6	800°
Gallium	5.91	29.75°	Sulfur (monoclinic) . . .	1.96	119.0°
Gold	19.3	1063°	Sulfur (rhombic)	2.07	112.8°
Iodine	4.93	113.5°	Tantalum	16.6	2996°
Iridium	22.4	2350°	Tellurium (metallic) . . .	6.24	452°
Iron	7.86	1535°	Tin (white, tetragonal) . .	7.31	231.85°
Lead	11.34	327.5°	Titanium	4.5	1800°
Lithium	0.53	186°	Tungsten	19.3	3370°
Magnesium	1.74	651°	Vanadium	5.96	1710°
Manganese	7.2	1260°	Zinc	7.14	419.43°

WEIGHT IN GRAMS OF 1 LITER OF VARIOUS GASES UNDER STANDARD CONDITIONS; BOILING POINTS UNDER PRESSURE OF 760 MILLIMETERS

NAME	WEIGHT OF 1 LITER	BOILING POINT	NAME	WEIGHT OF 1 LITER	BOILING POINT
Acetylene	1.1621	- 83.6°	Hydrogen chloride . . .	1.6398	- 85.0°
Air	1.2930	—	Hydrogen sulfide	1.5392	- 59.6°
Ammonia	0.7708	- 33.3°	Methane	0.7168	- 161.4°
Argon	1.7824	- 185.7°	Nitric oxide	1.3402	- 151.0°
Carbon dioxide	1.9768	sublimes	Nitrogen	1.2506	- 195.8°
Carbon monoxide	1.2504	- 192.0°	Nitrous oxide	1.9777	- 89.5°
Chlorine	3.214	- 34.6°	Oxygen	1.4290	- 183.0°
Helium	0.1785	- 268.9°	Sulfur dioxide	2.9266	- 10.0°
Hydrogen	0.08987	- 252.7°			

ELECTROMOTIVE SERIES

1. Lithium	7. Manganese	13. Nickel	19. Mercury
2. Potassium	8. Zinc	14. Tin	20. Silver
3. Calcium	9. Chromium	15. Lead	21. Platinum
4. Sodium	10. Iron	16. Hydrogen	22. Gold
5. Magnesium	11. Cadmium	17. Copper	
6. Aluminum	12. Cobalt	18. Arsenic, antimony, bismuth	

VAPOR PRESSURE OF WATER EXPRESSED IN
MILLIMETERS OF MERCURY

(International Critical Tables)

TEMPERATURE	PRESSURE	TEMPERATURE	PRESSURE	TEMPERATURE	PRESSURE
10°	9.209	21°	18.650	32°	35.663
11°	9.844	22°	19.827	33°	37.729
12°	10.518	23°	21.068	34°	39.898
13°	11.231	24°	22.377	35°	42.175
14°	11.987	25°	23.756	36°	44.563
15°	12.788	26°	25.209	37°	47.067
16°	13.634	27°	26.739	38°	49.692
17°	14.530	28°	28.349	39°	52.442
18°	15.477	29°	30.043	40°	55.324
19°	16.477	30°	31.824	50°	92.51
20°	17.535	31°	33.695	100°	760.00

RELATION BETWEEN ENGLISH AND METRIC CONSTANTS

1 lb (troy) = 373.24 g	1 gal (imperial) = 4.5460 l
1 oz (troy) = 31.10348 g	1 cc = 0.0610 cu in.
1 lb (avoirdupois) = 453.59 g	1 cu in. = 16.3872 cc
1 oz (avoirdupois) = 28.350 g	1 cu ft = 28,317 cc
1 kg = 2.67923 lb (troy)	1 cm = 0.3937 in.
1 kg = 2.20462 lb (avoirdupois)	1 m = 39.37 in.
1 l = 1.05668 United States liquid qt	1 km = 0.62137 miles
1 gal (U.S.) = 3.78543 l	

SOLUBILITIES OF SOME OF THE COMPOUNDS OF THE MORE COMMON METALS

	ACETATE	BROMIDE	CARBONATE	CHLORATE	CHLORIDE	CHROMATE	HYDROXIDE	IODIDE	NITRATE	OXIDE	PHOSPHATE	SILICATE (ORTHO)	SULFATE	SULFIDE
Aluminum	W	W		W	W		A	W	W	A-I	A	A-I	W	H-A
Ammonium	W	W	W	W	W	W	W	W	W		W		W	W
Barium	W	W	A	W	W	A	W	W	W	W	A	A	I	W
Calcium	W	W	A	W	W	W-A	W-A	W	W	W-A	A	A	W-I	W-A
Cobalt	W	W	A	W	W	A	A	W	W	A	A	A	W	A
Copper	W	W	A	W	W	W	A	A	W	A	A	A	W	A-N
Ferric	W	W		W	W	W	A	W	W	A	A	A	W	A
Ferrous	W	W	A	W	W		A	W	W	A	A	A	W	A
Lead	W	W-A	A	W	W-I	A-I	A	W-A	W	A	A	A	A-I	A
Magnesium	W	W	A	W	W	W	A	W	W	A	A	A	W	H-A
Manganese	W	W	A	W	W	A	A	W	W	A	A	A	W	A
Mercuric	W	W	A	W	W	W-A	A	A	W	A	A		H-A	A-R
Mercurous	W-A	A	H-A	W	A-I	A		A-N	W	A	A-N		W-A	A-I
Nickel	W	W	A	W	W	A	A	W	W	A	A	A	W	A
Potassium	W	W	W	W	W	W	W	W	W	W	W	W	W	W
Silver	W-A	I	H-A	W	I	A		I	W	A	A	A	W-A	A
Sodium	W	W	W	W	W	W	W	W	W	W	W	W	W	W
Stannous	W	W	A	W	W	A	A	W		A	A		W	A
Zinc	W	W	A	W	W	A	A	W	W	A	A	A	W	A

W, soluble in water.

A, insoluble in water, soluble in HCl or HNO₃, or both.

A-N, insoluble in water, soluble in HNO₃, and either insoluble in HCl or less soluble than in HNO₃.

I, insoluble in water, HCl, and HNO₃.

H, hydrolyzed by water.

W-A, slightly soluble in water, soluble in acids.

A-I, insoluble in water, slightly soluble in acids.

W-I, slightly soluble in water and in acids.

A-R, soluble only in aqua regia.

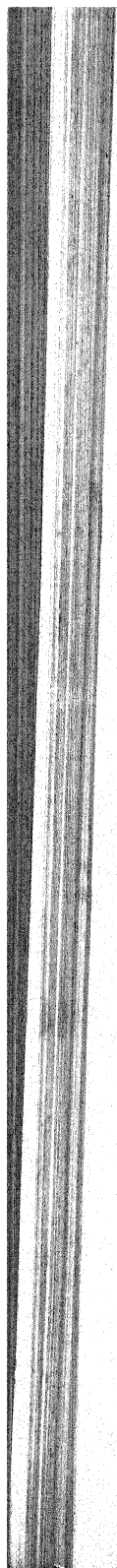
H-A, hydrolyzed by water, soluble in acids.

LIST OF STABLE ISOTOPES

Compiled from the Report of the Committee on Atoms of the International Union of Chemistry, published October, 1940. The isotopes of each element are listed in the order of abundance (the most abundant being given first). Values in parentheses lack verification. A dash — signifies that the element has no isotopes

ATOMIC NUMBER	SYMBOL OF ELEMENT AND ATOMIC WEIGHT	ISOTOPES (Mass Numbers)	ATOMIC NUMBER	SYMBOL OF ELEMENT AND ATOMIC WEIGHT	ISOTOPES (Mass Numbers)
1	H 1.0080	1, 2 *	44	Ru 101.7	102, 101, 104, 100,
2	He 4.003	—			99, 96, (98)
3	Li 6.940	7, 6	45	Rh 102.91	101, 103
4	Be 9.02	—	46	Pd 106.7	106, 108, 105, 110,
5	B 10.82	11, 10			104, 102
6	C 12.010	12, 13	47	Ag 107.880	107, 109
7	N 14.008	14, 15	48	Cd 112.41	114, 112, 111, 110,
8	O 16.000	16, 18, 17			113, 116, 106, 108
9	F 19.00	—	49	In 114.76	115, 113
10	Ne 20.183	20, 22, 21	50	Sn 118.70	120, 118, 116, 119,
11	Na 22.997	—			117, 124, 122,
12	Mg 24.32	24, 25, 26			112, 114, 115
13	Al 26.97	—	51	Sb 121.76	121, 123
14	Si 28.06	28, 29, 30	52	Te 127.61	130, 128, 126, 125,
15	P 30.98	—			124, 122, 123
16	S 32.06	32, 34, 33, (36)	53	I 126.92	—
17	Cl 35.457	35, 37	54	Xe 131.3	132, 129, 131, 134,
18	A 39.944	40, 36, 38			136, 130, 128,
19	K 39.096	39, 41, 40			124, 126
20	Ca 40.08	40, 44, 42, 48, 43, 46	55	Cs 132.91	—
21	Sc 45.10	—	56	Ba 137.36	138, 137, 136, 135,
22	Ti 47.90	48, 46, 47, 49, 50			134, 130, 132
23	V 50.95	—	57-71	Rare earths	—
24	Cr 52.01	52, 53, 50, 54	72	Hf 178.6	180, 178, 177, 179,
25	Mn 54.93	—			176, 174
26	Fe 55.85	56, 54, 57, 58	73	Ta 180.88	—
27	Co 58.94	59, 57	74	W 183.92	184, 186, 182, 183,
28	Ni 58.69	58, 60, 62, 64, 61			180
29	Cu 63.57	63, 65	75	Re 186.31	187, 185
30	Zn 65.38	64, 66, 68, 67, 70	76	Os 190.2	192, 190, 189, 188,
31	Ga 69.72	69, 71			187, 186, 184
32	Ge 72.60	74, 72, 70, 73, 76	77	Ir 193.1	193, 191
33	As 74.91	—	78	Pt 195.23	195, 194, 196, 198,
34	Se 78.96	80, 78, 76, 82, 77,			192
		74	79	Au 197.2	—
35	Br 79.916	79, 81	80	Hg 200.61	202, 200, 199, 201,
36	Kr 83.7	84, 86, 82, 83, 80,			198, 204, 196
		78	81	Tl 204.39	205, 203
37	Rb 85.48	85, 87	82	Pb 207.21	208, 206, 207, 204
38	Sr 87.63	88, 86, 87, 84	83	Bi 209.00	—
39	Y 88.92	—	90	Th 232.12	—
40	Zr 91.22	90, 92, 94, 91, 96	92	U 238.07	238, 235, 234
41	Cb 92.91	—			
42	Mo 95.95	98, 96, 95, 92, 94,			
		97, 100			

* Hydrogen of mass 2 is known as *deuterium*.



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